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THE OSMOTIC PRESSURE OF CANE SUGAR SOLUTIONS AT 20°.[1]

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The present series of 27 measurements of osmotic pressure was carried through without loss of concentration in any of the solutions while in the cells. After their removal from the cells they were all found to exhibit precisely the same rotation as other portions of the original solutions which had been reserved for polariscopic comparison at the conclusion of the experiments. In several of the more recent series of measurements, we had been able to avoid any sensible dilution in the lower concentrations of solution, but not in the higher ones. That we are now able to suppress all dilution of the cell contents is due to recent improvements in the cells which make it practicable to fill and close, and to open and empty them, so quickly that the solutions suffer no detectable dilution by water which is acquired from the porous walls. The abstraction of water from the cell walls, and, consequently, a dilution of the solution, occurs, of course, whenever the pressure upon

[1] The work upon osmotic pressure which is in progress in this laboratory is aided by grants from the Carnegie Institution. The earlier papers upon the subject will be found in THIS JOURNAL, **26**, 80; **28**, 1; **29**, 173; **32**, 93; **34**, 1; **36**, 1 and 39; **37**, 324, 425, and 558; **38**, 175; **39**, 667; **40**, 1, 194, 266, and 325; **41**, 1 and 92.

the latter is less than the maximum osmotic pressure. On this account, it was necessary to shorten greatly the time occupied in closing and opening the cells, and this has been reduced from 10 or 15 minutes to less than one minute by the improvements referred to, most of which were described in a former paper.[1]

The suppression of all dilution of the cell contents, whether weak or concentrated, is, without doubt, the most important single step forward which has been taken during our long continued endeavor to develop an accurate method for the measurement of osmotic pressure.

In this series (VIII.) at 20°, as in Series VII.[2] at 25°, there was no observable variation in bath temperature. This does not mean that the measurements are wholly free from *thermometer effects;* on the contrary, as will be seen in the records, most of them exhibit those slight fluctuations of pressure which we interpret as *thermometer effects* due to minute changes in the temperature of the solutions.

Unfortunately, the supply of the sugar with which the measurements at 10°, 15°, and 25° were made became exhausted before the series at 20° had been completed, and it was necessary to finish the work with other material. The sugar which was employed in the earlier work was a "rock candy," which, by analysis and by polariscopic examination, as well as by Fehling's test, was shown to be of exceptional purity. Hence no difficulty was anticipated in obtaining a new supply of suitable material of the same kind. But in this we were disappointed. Specimens of rock candy were procured from a number of different sources. All of them, however, were found to contain reducing sugars in such quantities as to render them unfit for our purpose. We then procured a quantity of "best" loaf sugar, and this was the material with which the series was completed. Its solutions gave very nearly the same rotations as those of the material which had previously been used, and the proportion of reducing sugar contained in it was—so far as we could determine by a series of comparative tests with Fehling's solution—less than one part in 1500. We

[1] THIS JOURNAL, **40**, 266.
[2] *Ibid.*, **41**, 1.

shall, however, have occasion in the latter part of this paper to call attention to the fact that the osmotic pressure of its solutions was slightly higher than we had expected.

The results at 20° are given in this paper in the usual forms. Tables I.–XXVII. present the individual measurements in some detail. In Table XXVIII., the results are summarized for each experiment, and in Table XXIX., for each concentration of solution. Tables XXX. and XXXI. are introduced to show how the series of measurements at 20° compares with the earlier series at other temperatures in respect to osmotic pressure and the ratio of osmotic to gas pressure.

Table I.

0.1 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 12°.7; (2) at conclusion of expr., 12°.7; loss, 0. *Manometer:* No. 11; volume of nitrogen, 381.11; displacement, 0 mm. Cell used, B_3. Resistance of membrane, 333,000. *Corrections:* (1) atmospheric pressure, 1.003; (2) liquids in manometer, 0.384; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 2.21. Time of setting up cell, 4 P.M., Dec. 14, 1908.

	Temperature.		Volume N_2.	Pressure.		
Time. Dec. 16.	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
12.30 P.M.	20°.00	20°.00	122.44	2.523	2.39	0.133
5.00 P.M.	20°.00	19°.95	122.57	2.521	"	0.131
10.00 P.M.	20°.00	20°.10	122.20	2.530	"	0.140
Dec. 17.						
2.30 P.M.	20°.00	20°.00	122.47	2.526	"	0.136
				2.525	2.39	0.135

Molecular osmotic pressure, 25.55.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.056.

Table II.

0.1 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 12°.7; (2) at conclusion of expr., 12°.7; loss, 0. *Manometer:* No. 20; volume of nitrogen, 409.01; displacement, 0 mm. Cell used, D_3. Resistance of membrane, 333,000. *Corrections:* (1) atmospheric pressure, 0.9974; (2) liquids in manometer, 0.44; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 2.51. Time of setting up cell, 4.00 P.M., Dec. 14, 1908.

	Temperature.		Volume N_2.	Pressure.		
Time.	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
Dec. 17.						
9.00 A.M.	20°.00	20°.00	133.18	2.528	2.39	0.138
2.00 P.M.	20°.00	20°.00	133.73	2.518	"	0.128
9.00 P.M.	20°.00	20°.00	133.81	2.519	"	0.129
Dec. 18.						
9.00 A.M.	20°.00	19°.80	134.57	2.512	"	0.122
				2.519	2.39	0.129

Molecular osmotic pressure, 25.19.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.054.

Table III.

0.2 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 24.95; (2) at conclusion of expr., 24°.95; loss, 0. *Manometer:* No. 6; volume of nitrogen, 620.8; displacement, 0. Cell used, F_3. Resistance of membrane, 333,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.45; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.90. Time of setting up cell, 3.30 P.M., Dec. 7, 1908.

	Temperature.		Volume N_2.	Pressure.		
Time.	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
Dec. 8.						
9.00 A.M.	20°.00	19°.95	111.57	5.03	4.78	0.25
12.30 P.M.	20°.00	20°.10	111.55	5.03	"	0.25
9.00 P.M.	20°.00	20°.10	111.90	5.02	"	0.24
Dec. 9.						
10.30 A.M.	20°.00	20°.00	111.49	5.03	"	0.25
				5.03	4.78	0.25

Molecular osmotic pressure, 25.15.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.052.

Table IV.

0.2 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 24°.95; (2) at conclusion of expr., 24°.95; loss, 0. *Manometer:* No. 20; volume of nitrogen, 409.01; displacement, 0. Cell used, G_3. Resistance of membrane, 170,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.52; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.34. Time of setting up cell, 3.30 P.M., Dec. 7, 1908.

Time.	Temperature. Solutions.	Temperature. Manometer.	Volume N_2.	Pressure. Osmotic.	Pressure. Gas.	Pressure. Difference.
Dec. 7.						
10.00 P.M.	20°.00	20°.00	74.60	5.02	4.78	0.24
Dec. 9.						
10.00 A.M.	20°.00	20°.00	74.65	5.02	"	0.24
2.30 P.M.	20°.00	20°.00	74.62	5.02	"	0.24
				5.02	4.78	0.24

Molecular osmotic pressure, 25.10.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.050.

Table V.

0.2 Wt. normal solution. Exp. No. 3. *Rotation:* (1) original, 24°.9; (2) at conclusion of expr., 24°.9; loss, 0. *Manometer:* No. 21; volume of nitrogen, 400.14; displacement, 0 mm. Cell used, G_3. Resistance of membrane, 180,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.56; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 4.86. Time of setting up cell, 4.00 P.M., Dec. 14, 1908.

Time.	Temperature. Solutions.	Temperature. Manometer.	Volume N_2.	Pressure. Osmotic.	Pressure. Gas.	Pressure. Difference.
Dec. 15.						
10.00 P.M.	20°.00	20°.00	73.25	5.04	4.78	0.26
Dec. 16.						
9.00 A.M.	20°.00	20°.00	73.50	5.01	"	0.23
12.30 P.M.	20°.00	20°.00	73.52	5.02	"	0.24
10.00 P.M.	20°.00	20°.10	73.77	5.00	"	0.22
				5.02	4.78	0.24

Molecular osmotic pressure, 25.09.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.050.

Table VI.

0.3 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 36°.65; (2) at conclusion of expr., 36°.65; loss, 0. *Manometer:* No. 11; volume of nitrogen, 381.11; displacement, 0 mm. Cell used, G_3. Resistance of membrane, 136,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.50; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 6.58. Time of setting up cell, 5.00 P.M., Nov. 27, 1908.

	Temperature.		Volume N_2.	Pressure.		
Time.	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
Nov. 28.						
9.00 A.M.	20°.00	19°.90	48.02	7.45	7.17	0.28
2.00 P.M.	20°.00	20°.00	48.04	7.44	"	0.27
11.30 P.M.	20°.00	20°.00	48.03	7.45	"	0.28
Nov. 29.						
10.00 A.M.	20°.00	20°.00	48.08	7.44	"	0.27
				7.45	7.17	0.28

Molecular osmotic pressure, 24.82.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.038.

Table VII.

0.3 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 36°.65; (2) at conclusion of expr., 36°.65; loss, 0. *Manometer:* No. 6; volume of nitrogen, 620.80; displacement, 0. Cell used, C_3. Resistance of membrane, 250,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.50; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 6.82. Time of setting up cell, 4.00 P.M., Dec. 14, 1908.

	Temperature.		Volume N_2.	Pressure.		
Time.	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
Dec. 15.						
5.00 P.M.	20°.00	20°.00	78.27	7.45	7.17	0.28
10.00 P.M.	20°.00	20°.00	78.25	7.45	"	0.28
Dec. 16.						
10.00 P.M.	20°.00	20°.10	78.12	7.46	"	0.29
Dec. 17.						
9.00 A.M.	20°.00	20°.00	78.17	7.45	"	0.28
				7.45	7.17	0.28

Molecular osmotic pressure, 24.84.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.038.

Table VIII.

0.4 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 48°.1; (2) at conclusion of expr., 48°.1; loss, 0. *Manometer:* No. 11; volume of nitrogen, 381.11; displacement, 0. Cell used, C_3. Resistance of membrane, 500,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.52; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 8.52. Time of setting up cell, 5.00 P.M., Nov. 7, 1908.

Time.	Temperature. Solutions.	Temperature. Manometer.	Volume N_2.	Pressure. Osmotic.	Pressure. Gas.	Pressure. Difference.
Nov. 8.						
9.30 A.M.	20°.00	20°.00	36.66	9.96	9.56	0.40
10.00 P.M.	20°.00	20°.10	36.45	10.01	"	0.45
Nov. 9.						
9.00 A.M.	20°.00	20°.00	36.54	9.98	"	0.42
				9.98	9.56	0.42

Molecular osmotic pressure, 24.96.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.044.

Table IX.

0.4 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original 48°.15; (2) at conclusion of expr., 48°.15; loss, 0. *Manometer:* No. 11; volume of nitrogen, 381.11; displacement, 0. Cell used, G_3. Resistance of membrane, 225,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.52; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 9.57. Time of setting up cell, 5.00 P.M., Nov. 9, 1908.

Time.	Temperature. Solutions.	Temperature. Manometer.	Volume N_2.	Pressure. Osmotic.	Pressure. Gas.	Pressure. Difference.
Nov. 10.						
9.00 A.M.	20°.00	20°.00	36.59	9.96	9.56	0.40
1.00 P.M.	20°.00	20°.00	36.66	9.94	"	0.38
5.00 P.M.	20°.20	20°.20	36.65	9.94	"	0.38
Nov. 11.						
9.00 A.M.	20°.00	20°.00	36.71	9.92	"	0.36
				9.94	9.56	0.38

Molecular osmotic pressure, 24.85.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.040.

Table X.

0.4 Wt. normal solution. Exp. No. 3. *Rotation:* (1) original, 48°.0; (2) at conclusion of expr., 48°.0; loss, 0. *Manometer:* No. 6; volume of nitrogen, 620.80; displacement, 0. Cell used, F_3. Resistance of membrane, 333,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.51; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 3.00. Time of setting up cell, 4.00 P.M., Dec. 2, 1908.

	Temperature.		Volume N_2.	Pressure.		
Time.	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
Dec. 3.						
5.00 P.M.	20°.00	20°.00	59.27	9.98	9.56	0.42
Dec. 4.						
9.00 A.M.	20°.00	20°.00	59.43	9.98	"	0.42
12.30 P.M.	20°.00	20°.00	59.60	9.95	"	0.39
4.00 P.M.	20°.00	20°.00	59.58	9.95	"	0.39
				9.97	9.56	0.41

Molecular osmotic pressure, 24.91.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.042.

Table XI.

0.5 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 58°.8; (2) at conclusion of expr., 58°.8; loss, 0. *Manometer:* No. 20; volume of nitrogen, 416.72; displacement, 0. Cell used, E_3. Resistance of membrane, 110,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.58; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 12.38. Time of setting up cell, 4.30 P.M., Nov. 2, 1908.

	Temperature.		Volume N_2.	Pressure.		
Time.	Solutions.	Manometer.		Osmotic.	Gas.	Difference.
Nov. 3.						
5.00 P.M.	20°.00	20°.20	32.31	12.48	11.95	0.53
11.30 P.M.	20°.00	20°.00	32.31	12.49	"	0.54
Nov. 4.						
8.30 A.M.	20°.00	20°.00	32.31	12.50	"	0.55
4.00 P.M.	20°.00	20°.00	32.34	12.49	"	0.54
				12.49	11.95	0.54

Molecular osmotic pressure, 24.98.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.045.

Table XII.

0.5 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 58°.7; (2) at conclusion of expr., 58°.7; loss, 0. *Manometer:* No. 5; volume of nitrogen, 446.45; displacement, 0. Cell used, F_3. Resistance of membrane, 272,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 10.74. Time of setting up cell, 5.00 P.M., Nov. 27, 1908.

Time.	Temperature. Solutions.	Temperature. Manometer.	Volume N_2.	Pressure. Osmotic.	Pressure. Gas.	Pressure. Difference.
Nov. 28.						
2.00 P.M.	20°.00	20°.00	34.71	12.48	11.95	0.53
11.30 P.M.	20°.00	20°.00	34.64	12.51	"	0.56
Nov. 29.						
10.00 A.M.	20°.00	20°.00	34.68	12.49	"	0.54
Nov. 30.						
9.00 A.M.	20°.00	20°.00	34.71	12.49	"	0.54
				12.49	11.95	0.54

Molecular osmotic pressure, 24.98.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.045.

Table XIII.

0.5 Wt. normal solution. Exp. No. 3. *Rotation:* (1) original, 58°.9; (2) at conclusion of expr., 58°.9; loss, 0. *Manometer:* No. 21; volume of nitrogen, 400.14; displacement, 0. Cell used, C_3. Resistance of membrane, 182,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 11.84. Time of setting up cell, 4.00 P.M., Nov. 30, 1908.

Time.	Temperature. Solutions.	Temperature. Manometer.	Volume N_2.	Pressure. Osmotic.	Pressure. Gas.	Pressure. Difference.
Dec. 2.						
10.00 P.M.	20°.00	20°.00	31.09	12.50	11.95	0.55
Dec. 3.						
9.00 A.M.	20°.00	20°.00	31.09	12.49	"	0.56
11.00 P.M.	20°.00	20°.00	31.10	12.50	"	0.55
Dec. 4.						
4.00 P.M.	20°.00	20°.00	31.11	12.50	"	0.55
				12.50	11.95	0.55

Molecular osmotic pressure, 25.00.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.046.

Table XIV.

0.6 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 69°.4; (2) at conclusion of expr., 69°.4; loss, 0. *Manometer:* No. 11; volume of nitrogen, 381.11; displacement, 0. Cell used, C_3. Resistance of membrane, 500,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.54; (3) dilution, 0; (4) concentration, 0; (5) capillary depression 0.02. Initial pressure, 14.57. Time of setting up cell, 4.30 P.M., Nov. 3, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solutions.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Nov. 4.						
9.00 P.M.	20°.00	20°.20	24.41	15.15	14.34	0.81
Nov. 5.						
5.00 P.M.	20°.00	20°.20	24.38	15.17	"	0.83
9.00 P.M.	20°.00	20°.20	24.34	15.20	"	0.86
Nov. 6.						
8.30 A.M.	20°.00	20°.00	24.37	15.18	"	0.84
				15.18	14.34	0.84

Molecular osmotic pressure, 25.29.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.058.

Table XV.

0.6 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 69°.5; (2) at conclusion of expr., 69°.5; loss, 0. *Manometer:* No. 13; volume of nitrogen, 432.28; displacement, 0. Cell used, B_3. Resistance of membrane, 330,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.62; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 14.50. Time of setting up cell, 5.00 P.M., Nov. 4, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solutions.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Nov. 5.						
9.00 A.M.	20°.00	20°.00	27.73	15.22	14.34	0.88
12.30 P.M.	20°.00	20°.00	27.72	15.22	"	0.88
9.00 P.M.	20°.00	20°.00	27.72	15.22	"	0.88
Nov. 6.						
8.30 A.M.	20°.00	20°.00	27.75	15.21	"	0.87
				15.22	14.34	0.88

Molecular osmotic pressure, 25.36.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.061.

Table XVI.

0.7 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 79°.4; (2) at conclusion of expr., 79°.4; loss, 0. *Manometer:* No. 13; volume of nitrogen, 432.33; displacement, 0. Cell used, A_3. Resistance of membrane, 225,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.62; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.71. Time of setting up cell, 3.00 P.M., Nov. 6, 1908.

Time.	Temperature. Solutions.	Temperature. Manometer.	Volume N_2.	Pressure. Osmotic.	Pressure. Gas.	Pressure. Difference.
Nov. 7.						
9.00 A.M.	20°.00	20°.20	23.78	17.83	16.73	0.10
1.00 P.M.	20°.00	20°.00	23.78	17.83	"	0.10
4.30 P.M.	20°.00	20°.00	23.79	17.82	"	0.09
Nov. 8.						
9.30 A.M.	20°.00	20°.00	23.79	17.83	"	0.10
				17.83	16.73	0.10

Molecular osmotic pressure, 25.47.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.066.

Table XVII.

0.7 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 79°.3; (2) at conclusion of expr., 79°.3; loss, 0. *Manometer:* No. 5; volume of nitrogen, 446.45; displacement, 0. Cell used, D_3. Resistance of membrane, 150,000. *Corrections:* (1) atmospheric pressure, 1.005; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.61. Time of setting up cell, 3.30 P.M., Dec. 8, 1908.

Time.	Temperature. Solutions.	Temperature. Manometer.	Volume N_2.	Pressure. Osmotic.	Pressure. Gas.	Pressure. Difference.
Dec. 9.						
9.00 A.M.	20°.00	20°.00	24.53	17.83	16.73	1.10
2.00 P.M.	20°.00	20°.00	24.52	17.84	"	1.11
9.30 P.M.	20°.00	20°.00	24.48	17.86	"	1.13
Dec. 10.						
9.00 A.M.	20°.00	20°.00	24.49	17.85	"	1.12
				17.85	16.73	1.12

Molecular osmotic pressure, 25.49.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.067.

Table XVIII.

0.7 Wt. normal solution. Exp. No. 3. *Rotation:* (1) original, 79°.3; (2) at conclusion of expr., 79°.3; loss, 0. *Manometer:* No. 21; volume of nitrogen, 400.14; displacement, 0. Cell used, F_3. Resistance of membrane, 275,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.63; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 16.66. Time of setting up cell, 4.00 P.M., Dec. 21, 1908.

Time.	Temperature. Solutions.	Manometer.	Volume N_2.	Pressure. Osmotic.	Gas.	Difference.
Dec. 22.						
1.00 P.M.	20°.00	20°.00	22.01	17.82	16.73	1.09
10.00 P.M.	20°.00	20°.00	22.01	17.83	"	1.10
Dec. 23.						
9.00 P.M.	20°.00	20°.10	22.00	17.83	"	1.10
12.30 P.M.	20°.00	20°.00	22.01	17.82	"	1.09
				17.83	16.73	1.10

Molecular osmotic pressure, 25.46.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.065.

Table XIX.

0.8 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 89°.25; (2) at conclusion of expr., 89°.25; loss, 0. *Manometer:* No. 11; volume of nitrogen, 381.11; displacement, 0. Cell used, A_3. Resistance of membrane, 162,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.54; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 20.36. Time of setting up cell, 4.00 P.M., Nov. 21, 1908.

Time.	Temperature. Solutions.	Manometer.	Volume N_2.	Pressure. Osmotic.	Gas.	Difference.
Nov. 21.						
11.00 P.M.	20°.00	20°.20	18.13	20.58	19.12	1.46
Nov. 22.						
10.30 A.M.	20°.00	20°.00	18.07	20.64	"	1.52
Nov. 23.						
9.00 A.M.	20°.00	20°.10	18.09	20.62	"	1.50
12.30 P.M.	20°.00	19°.90	18.08	20.62	"	1.50
				20.62	19.12	1.50

Molecular osmotic pressure, 25.76.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.078.

Table XX.

0.8 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 89°.25; (2) at conclusion of expr., 89°.25; loss, 0. *Manometer:* No. 5; volume of nitrogen, 446.45; displacement, 0. Cell used, G_3. Resistance of membrane, 160,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.62; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 20.50. Time of setting up cell, 4.00 P.M., Dec. 2, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solutions.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Dec. 3.						
8.00 P.M.	20°.00	20°.00	21.31	20.58	19.12	1.46
Dec. 4.						
9.00 A.M.	20°.00	20°.00	21.32	20.58	"	1.46
12.00 M.	20°.00	20°.00	21.35	20.55	"	1.43
4.00 P.M.	20°.00	20°.00	21.33	20.58	"	1.46
				20.57	19.12	1.45

Molecular osmotic pressure, 25.72.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.076.

Table XXI.

0.8 Wt. normal solution. Exp. No. 3. *Rotation:* (1) original, 89°.15; (2) at conclusion of expr., 89°.15; loss, 0. *Manometer:* No. 22; volume of nitrogen, 416.14; displacement, 0. Cell used, C_3. Resistance of membrane, 220,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.60; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.59. Time of setting up cell, 4.00 P.M., Dec. 18, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solutions.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Dec. 19.						
8.30 P.M.	20°.00	20°.05	19.81	20.63	19.12	1.51
Dec. 20.						
8.30 P.M.	20°.00	19°.80	19.83	20.61	"	1.49
Dec. 21.						
1.00 P.M.	20°.00	20°.00	19.83	20.61	"	1.49
Dec. 22.						
9.00 A.M.	20°.00	20°.00	19.82	20.61	"	1.49
				20.62	19.12	1.50

Molecular osmotic pressure, 25.77.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.078.

Table XXII.

0.9 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 98°.5; (2) at conclusion of expr., 98°.5; loss, 0. *Manometer:* No. 6; volume of nitrogen, 620.8; displacement, 0. Cell used, D_3. Resistance of membrane, 157,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.57; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 22.77. Time of setting up cell, 2.30 P.M., Dec. 5, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solutions.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Dec. 6.						
3.00 P.M.	20°.00	20°.00	26.10	23.36	21.51	1.85
9.00 P.M.	20°.00	20°.00	26.10	23.37	"	1.86
Dec. 7.						
9.00 A.M.	20°.00	20°.00	26.12	23.36	"	1.85
2.30 P.M.	20°.00	20°.00	26.13	23.35	"	1.84
				23.36	21.51	1.85

Molecular osmotic pressure, 25.96.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.086.

Table XXIII.

0.9 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 98°.3; (2) at conclusion of expr., 98°.3; loss, 0. *Manometer:* No. 5; volume of nitrogen, 446.45; displacement, 0. Cell used, F_3. Resistance of membrane, 550,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.60; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 19.92. Time of setting up cell, 4.00 P.M., Dec. 17, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solutions.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Dec. 18.						
12.30 P.M.	20°.00	20°.00	18.84	23.34	21.51	1.83
8.30 P.M.	20°.00	20°.00	18.85	23.32	"	1.81
Dec. 19.						
10.30 A.M.	20°.00	20°.00	18.87	23.28	"	1.77
2.00 P.M.	20°.00	20°.00	18.86	23.29	"	1.78
				23.31	21.51	1.80

Molecular osmotic pressure, 25.90.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.084.

Table XXIV.

0.9 Wt. normal solution. Exp. No. 3. *Rotation:* (1) original, 98°.3; (2) at conclusion of expr., 98°.3; loss, 0. *Manometer:* No. 6; volume of nitrogen, 620.8; displacement, 0. Cell used, A_3. Resistance of membrane, 135,000. *Corrections:* (1) atmospheric pressure, 0.99; (2) liquids in manometer, 0.57; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 19.47. Time of setting up cell, 4.00 P.M., Dec. 17, 1908.

Time.	Temperature. Solutions.	Temperature. Manometer.	Volume N_2.	Pressure. Osmotic.	Pressure. Gas.	Pressure. Difference.
Dec. 18.						
9.00 A.M.	20°.00	19°.80	26.22	23.27	21.51	1.76
8.30 P.M.	20°.00	20°.00	26.22	23.27	"	1.76
Dec. 19.						
10.30 A.M.	20°.00	20°.00	26.21	23.27	"	1.76
2.00 P.M.	20°.00	20°.00	26.20	23.27	"	1.76
				23.27	21.51	1.76

Molecular osmotic pressure, 25.86.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.082.

Table XXV.

1.00 Wt. normal solution. Exp. No. 1. *Rotation:* (1) original, 107°.45; (2) at conclusion of expr., 107°.45; loss, 0. *Manometer:* No. 22; volume of nitrogen, 416.14; displacement, 0. Cell used, B_3. Resistance of membrane, 300,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.61; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 25.60. Time of setting up cell, 4.00 P.M., Dec. 3, 1908.

Time.	Temperature. Solutions.	Temperature. Manometer.	Volume N_2.	Pressure. Osmotic.	Pressure. Gas.	Pressure. Difference.
Dec. 4.						
12.30 P.M.	20°.00	20°.00	15.71	26.12	23.90	2.22
11.30 P.M.	20°.00	20°.00	15.72	26.10	"	2.20
Dec. 5.						
8.30 A.M.	20°.00	19°.95	15.72	26.10	"	2.20
1.00 P.M.	20°.00	20°.00	15.70	26.14	"	2.24
				26.12	23.90	2.22

Molecular osmotic pressure, 26.12.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.093.

Table XXVI.

1.00 Wt. normal solution. Exp. No. 2. *Rotation:* (1) original, 107°.45; (2) at conclusion of expr., 107°.45; loss, 0. *Manometer:* No. 20; volume of nitrogen, 409.01; displacement, 0. Cell used, G_3. Resistance of membrane, 143,000. *Corrections:* (1) atmospheric pressure, 1.00; (2) liquids in manometer, 0.60; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 17.64. Time of setting up cell, 4.00 P.M., Dec. 18, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solutions.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Dec. 20.						
8.30 P.M.	20°.00	19°.80	15.44	26.12	23.90	2.22
Dec. 21.						
9.00 A.M.	20°.00	20°.00	15.43	26.13	"	2.23
5.00 P.M.	20°.00	20°.00	15.43	26.13	"	2.23
10.00 P.M.	20°.00	20°.00	15.42	26.14	"	2.24
				26.13	23.90	2.23

Molecular osmotic pressure, 26.13.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.093.

Table XXVII.

1.00 Wt. normal solution. Exp. No. 3. *Rotation:* (1) original, 107°.4; (2) at conclusion of expr., 107°.4; loss, 0. *Manometer:* No. 6; volume of nitrogen, 620.8; displacement, 0. Cell used, B_3. Resistance of membrane, 183,000. *Corrections:* (1) atmospheric pressure, 1.01; (2) liquids in manometer, 0.57; (3) dilution, 0; (4) concentration, 0; (5) capillary depression, 0.02. Initial pressure, 24.27. Time of setting up cell, 4.00 P.M., Dec. 21, 1908.

	Temperature.		Volume	Pressure.		
Time.	Solutions.	Manometer.	N_2.	Osmotic.	Gas.	Difference.
Dec. 22.						
1.00 P.M.	20°.00	20°.00	23.40	26.11	23.90	2.21
10.30 P.M.	20°.00	20°.00	23.40	26.12	"	2.22
Dec. 23.						
9.00 A.M.	20°.00	20°.10	23.40	26.11	"	2.21
12.30 P.M.	20°.00	20°.00	23.40	26.11	"	2.21
				26.11	23.90	2.21

Molecular osmotic pressure, 26.11.
Molecular gas pressure, 23.90.
Ratio of osmotic to gas pressure, 1.093.

Table XXVIII.—Summary of Results at 20°.

Weight normal concentration.	Osmotic pressure.	Gas pressure.	Difference	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	2.525	2.39	0.135	25.25	23.90	1.056
"	2.519	"	0.129	25.19	"	1.054
0.2	5.03	4.78	0.25	25.15	"	1.052
"	5.02	"	0.24	25.10	"	1.051
"	5.02	"	0.24	25.09	"	1.050
0.3	7.45	7.17	0.28	24.82	"	1.038
"	7.45	"	0.28	24.84	"	1.038
0.4	9.98	9.56	0.42	24.96	"	1.044
"	9.94	"	0.38	24.85	"	1.040
"	9.97	"	0.41	24.91	"	1.042
0.5	12.49	11.95	0.54	24.98	"	1.045
"	12.49	"	0.54	24.98	"	1.045
"	12.50	"	0.55	25.00	"	1.046
0.6	15.18	14.34	0.84	25.29	"	1.058
"	15.22	"	0.88	25.36	"	1.061
0.7	17.83	16.73	1.10	25.47	"	1.066
"	17.85	"	1.12	25.49	"	1.067
"	17.83	"	1.10	25.46	"	1.065
0.8	20.62	19.12	1.50	25.76	"	1.078
"	20.57	"	1.45	25.72	"	1.076
"	20.62	"	1.50	25.77	"	1.078
0.9	23.36	21.51	1.85	25.96	"	1.086
"	23.31	"	1.80	25.90	"	1.084
"	23.27	"	1.76	25.86	"	1.082
1.0	26.12	23.90	2.22	26.12	"	1.093
"	26.13	"	2.23	26.13	"	1.093
"	26.11	"	2.21	26.11	"	1.093

Table XXIX.—Summary of Results at 20°. Mean Values.

Weight normal concentration.	Osmotic pressure.	Gas pressure.	Difference.	Molecular osmotic pressure.	Molecular gas pressure.	Ratio of osmotic to gas pressure.
0.1	2.522	2.39	0.132	25.22	23.90	1.055
0.2	5.023	4.78	0.243	25.11	"	1.051
0.3	7.45	7.17	0.28	24.83	"	1.038
0.4	9.96	9.56	0.40	24.91	"	1.042
0.5	12.49	11.95	0.54	24.99	"	1.045
0.6	15.20	14.34	0.86	25.33	"	1.060
0.7	17.84	16.73	1.11	25.47	"	1.066
0.8	20.60	19.12	1.48	25.75	"	1.077
0.9	23.31	21.51	1.80	25.91	"	1.084
1.0	26.12	23.90	2.22	26.12	"	1.093

Table XXX.—Osmotic Pressures. Series III.–VIII.

Weight normal concentration.	Series III. Pressures. 0°.	Series IV. Pressures. 4°–5°.	Series V. Pressures. 10°.	Series VI. Pressures. 15°.	Series VIII. Pressures. 20°.	Series VII. Pressures. 25°.
0.1	2.42	2.40	2.44	2.48	2.52	2.56
0.2	4.79	4.75	4.82	4.91	5.02	5.10
0.3	7.11	7.07	7.19	7.33	7.45	7.57
0.4	9.35	9.43	9.58	9.78	9.96	10.12
0.5	11.75	11.82	12.00	12.29	12.49	12.73
0.6	14.12	14.43	14.54	14.86	15.20	15.42
0.7	16.68	16.79	17.09	17.39	17.84	18.02
0.8	19.15	19.31	19.75	20.09	20.60	20.73
0.9	21.89	22.15	22.28	22.94	23.31	23.66
1.0	24.45	24.53	25.06	25.42	26.12	26.33
1. Total pressure	131.71	132.68	134.75	137.49	140.52	142.24
2. Mean ratio of osmotic to gas pressure	1.074	1.065	1.061	1.064	1.069	1.064
3. Mean loss in rotation (per cent)	1.73	1.45	0.22	0.10	0.00	0.20

Table XXXI.—Mean Ratios of Osmotic to Gas Pressures. Sereis III.—VIII.

Weight normal concentration.	Series III. Ratios. 0°.	Series IV. Ratios. 4°–5°.	Series V. Ratios. 10°.	Series VI. Ratios. 15°.
0.1	1.085	1.060	1.056	1.053
0.2	1.074	1.045	1.043	1.045
0.3	1.064	1.041	1.038	1.040
0.4	1.049	1.042	1.037	1.040
0.5	1.055	1.043	1.040	1.046
0.6	1.056	1.059	1.050	1.055
0.7	1.070	1.060	1.058	1.058
0.8	1.074	1.067	1.069	1.069
0.9	1.091	1.081	1.073	1.085
1.0	1.097	1.084	1.085	1.083

Weight normal concentration.	Series VIII. Ratios. 20°.	Series VII. Ratios. 25°.	Series V.–VIII. Mean ratios.	
0.1	1.055	1.053	1.054	.....
0.2	1.051	1.048	1.047	.....
0.3	1.038	1.038	1.039	.....
0.4	1.042	1.041	1.040	.....
0.5	1.045	1.048	1.045	.....
0.6	1.060	1.058	1.056	.....
0.7	1.066	1.059	1.060	.....
0.8	1.077	1.066	1.070	.....
0.9	1.084	1.082	1.081	.....
1.0	1.093	1.084	1.086	.....

If Table XXX. is examined, it will be seen (horizontal line No. 1) that the aggregate pressure of Series VIII. at 20° is 140.52 atmospheres, while those of Series VI. at 15° and of Series VII. at 25° are 137.49 and 142.24 atmospheres, respectively. The total pressure which would have been expected for Series VIII.—if the temperature coefficient of osmotic pressure is equal to that of gases—is about 139.87 atmospheres. In other words, the series, considered as a unit, gave a pressure greater by 0.65 atmosphere than is consistent with its temperature relation to Series VI. at 15° and Series VII. at 25°. The same fact is brought out still more clearly by the ratios of osmotic to gas pressures given in horizontal line No. 2 (Table XXX.). It will there be seen that this ratio for Series VI. at 15°, and for Series VII. at 25°, is 1.084; while for Series

VIII. at 20°, it is 1.089, *i. e.*, one-half per cent higher than would have been expected if osmotic pressure obeys the law of Gay-Lussac for gases. We do not permit ourselves as yet to entertain any "*views*" regarding the proper magnitude of osmotic pressure at any temperature; nevertheless, we are prepared to state that all the best experimental evidence which we are securing is tending strongly in the direction of establishing the substantial equivalence of the temperature coefficients of osmotic and gas pressures, and that the major portion of the discrepancy, to which attention has been drawn, is easily explained without calling this equivalence into question. It was noted that, as long as the old supply of sugar was employed, the ratios of osmotic to gas pressure at 20° agreed well with those which had been found at 15° and 25°, but that these ratios increased as soon as the new material was brought into use. It would seem, therefore, that the difference in question was due, in large part, to the impurities of the new material. It was noted, also, that the increase in the ratio of osmotic to gas pressure which followed the introduction of the new supply of sugar was, as a rule, relatively greater in the higher concentrations of solution, *i. e.*, in those concentrations which, in all the earlier work, had suffered some dilution while in the cells. The meaning of the latter observation is clear. It signifies that the ratios hitherto obtained are probably somewhat too low in those cases in which dilution of the cell contents occurred.

JOHNS HOPKINS UNIVERSITY,
January 15, 1909.

THE ABSORPTION SPECTRA OF SOLUTIONS OF A NUMBER OF SALTS IN WATER, IN CERTAIN NONAQUEOUS SOLVENTS, AND IN MIXTURES OF THESE SOLVENTS.

[TWENTY-FOURTH COMMUNICATION.]

BY HARRY C. JONES AND JOHN A. ANDERSON.

[*Continued from March Number.*]

SALTS OF NEODYMIUM, PRASEODYMIUM, AND ERBIUM.

Some of the more important investigations on the salts of the above-named elements are the following:

Bahr and Bunsen[1] included didymium and erbium in their early work on absorption spectra.

Becquerel,[2] in his study of spectra in the infrared region, worked with didymium. In his subseqeunt work[3] on the variation of absorption spectra in crystals, the sulphate and nitrate of didymium were included.

Becquerel[4] compared the absorption spectra of crystals of didymium salts with the spectra of the aqueous solution of the same salts. He showed that from the displacement of the bands he could recognize distinct substances or definite compounds, and that in the crystals we may have, simultaneously, mixtures of different compounds and especially basic salts.

Demarcay[5] studied the spectrum of didymium, and concluded that in addition to praseodymium and neodymium a third element was probably present. In a subsequent investigation[6] he shows that neodymium from entirely different minerals and sources always has the same spectrum, and concludes that it is a chemical element.

Krüss and Wilson[7] carried out an elaborate investigation on the absorption spectra of the rare earths. They concluded that we must assume the existence of more than twenty elements in the various rare earth minerals.

Bettendorff[8] carried out three investigations on the spectra of the cerium and yttrium group, and Schottländer[9] made use of his spectroscopic studies and spectrophotometric work to characterize the various rare earths.

Boudouard[10] effected the separation of neodymium and praseodymium by means of potassium sulphate instead of ammonium nitrate. The absorption spectra indicated that the separation was nearly complete.

[1] Ann. Chem. (Liebig), **137,** 1 (1886).
[2] Ann. Chim. Phys. [5], **30,** 5 (1883).
[3] *Ibid.* [6], **14,** 170 (1888).
[4] *Ibid.*, [6], **14,** 257 (1888).
[5] Compt. rend., **102,** 1551 (1886); **105,** 276 (1887).
[6] *Ibid.*, **126,** 1040 (1898).
[7] Ber. d. chem. Ges., **20,** 2134 (1887).
[8] Ann. Chem. (Liebig), **256,** 159 (1890); **263,** 164 (1891); **270,** 376 (1892).
[9] Ber. d. chem. Ges., **25,** 569 (1892).
[10] Compt. rend., **126,** 900 (1898).

Scheele[1] did some very careful work on praseodymium in connection with his determination of the atomic weight of that element, and later[2] in connection with the separation of praseodymium and neodymium.

The elaborate investigations of Muthmann[3] and his coworkers, Stützel, Böhm, Baur, Hofer, and Weiss, call for special comment. These authors raise the question as to the elementary nature of praseodymium and neodymium, and point out certain lines of evidence, based on spectrum analysis, which make it not impossible that these substances are mixtures. They show that by spectrum analysis it is possible to determine approximately the amounts of neodymium and praseodymium in a mixture of the two, a fact which had earlier been utilized by Jones[4] in his work on the atomic weights of these two elements.

By the electrolysis of fused neodymium compounds Muthmann was able to prepare the pure metal. He then studied the physical properties not only of neodymium, but also of cerium, lanthanum, and praseodymium, which were prepared in the same manner.

An important and interesting investigation was carried out by Liveing[5] on the effects of dilution, temperature, nature of the solvent, etc., on the absorption spectra of solutions of didymium and erbium salts. His eye observations were made with an ordinary spectroscope, and the photographs also with a prism spectroscope. He obtained some very good plates, indeed, considering the kind of apparatus employed. He studied the effect on the absorption of increasing the dilution of the solution, and established the four following facts:

The spectra of the different salts of the same metal in dilute solution are identical. The spectrum is constant for the chloride and sulphate in different dilutions, as long as the thickness of the absorbing solutions is proportional to the

[1] Z. anorg. Chem., **17**, 310 (1898).

[2] Ber. d. chem. Ges., **32**, 409 (1899).

[3] Ber. d. chem. Ges., **32**, 2653 (1899); **33**, 42, 1748, 2028 (1900); Ann. Chem. (Liebig), **320**, 231 (1902).

[4] This Journal, **20**, 345 (1898).

[5] Camb. Phil. Soc., **18**, 298 (1900).

dilution. The spectrum of the nitrate is modified by some cause with increasing concentration.

The absorption of the short wave lengths, which differs for different salts, diminishes with increased dilution. Rise in temperature from about 20° to 97° renders the bands more diffuse, but does not increase their intensity. The addition of acid made the absorption in general more diffuse, but did not weaken the absorption.

From these facts Liveing concluded that absorption cannot be accounted for on the basis of electrolytic dissociation.

His work on absorption in nonaqueous solvents is of special interest in the present connection.

He states that didymium chloride dried at a temperature above 100° is quite insoluble in alcohol. This was doubtless due to the formation of the basic chloride. This salt can be heated to 140° to 150° in a current of dry hydrochloric acid gas, and the anhydrous salt is still completely soluble in alcohol. The salt with which he worked doubtless contained more or less water.

He says, further, that the absorption spectrum of the alcoholic solution shows the same bands as that of an aqueous solution, but they are somewhat modified. The positions of maximum absorption are all moved towards the red. The shift of the different bands is not equal. The bands in the yellow and green in the alcoholic solution are so shifted as to suggest the appearance of new bands, but Liveing states that by studying solutions of different concentrations he has convinced himself that no new bands appear. We shall see that this is an error.

He found that glycerol produced the same changes as alcohol in the spectrum of aqueous solutions. He closes thus:[1]

"On a review of the whole series of observations, I conclude that the characteristic absorption of didymium compounds, namely, those which are common to dilute aqueous solutions, and are only modified by concentration, by heat, and by variations of the solvent, are due to molecules which are iden-

[1] Camb. Phil. Soc., **18**, 314 (1900).

tical in all cases, though their vibrations are modified by their relations to other molecules surrounding them."

Urbain[1] devised a new method for separating the rare earths, using ethyl sulphate.

Drossbach,[2] in his work on absorption in the region of the ultraviolet, measured a number of the bands of praseodymium and neodymium; and Hartley[3] included the nitrate of erbium in his investigation on the absorption spectra of metallic nitrates. In the discussion of his results, Hartley calls attention to the fact that Bunsen[4] found that didymium salts in the crystallized state and in solution show absorption bands that vary in width with the thickness of the absorbing medium and with the quantity of the salt. Solutions of the chloride, sulphate, and acetate, each containing the same weight of didymium, yielded different spectra, the bands being shifted towards the red end of the spectrum with increase in the molecular weight of the salt.

Hartley points out that more recently Becquerel[5] observed similar variation in the absorption spectra, both in crystals and in solutions; while Muthmann and Stützel[6] found marked differences between the spectra of solutions of the different salts of neodymium, such as the chloride, nitrate, and carbonate.

As Hartley points out, these facts cannot be reconciled with the theory that the absorption spectra of solutions of neodymium salts are due to the neodymium ion, since the solutions of the above-named salts contain, for comparable concentrations, practically the same number of neodymium ions. He then concludes his paper with the paragraph already quoted. Among the more recent investigations on the salts of the rare earths is that of Miss Helen Schaeffer.[7] She attempted to test Kundt's law for the nitrates of certain rare earths, such as neodymium and cerium. She employed the

[1] Compt. rend., **126,** 835; **127,** 107 (1898).
[2] Ber. d. chem. Ges., **35,** 1486 (1902); Ann. Chim. Phys. [7], **19,** 184 (1900).
[3] J. Chem. Soc., **83,** 221 (1903).
[4] Pogg. Ann., **138,** 100 (1866).
[5] Compt. rend., **104,** 777, 1691 (1887).
[6] Ber. d. chem. Ges., **32,** 2653 (1899).
[7] Physik. Z., **7,** 822 (1906).

following solvents: Water, methyl alcohol, ethyl alcohol, propyl alcohol, isobutyl alcohol, amyl alcohol, allyl alcohol, glycerol, and acetone. Solutions containing 1 gram of the salt in 10 cc. of the solvent were used. She found that, in general, the bands had a different arrangement in the various solvents, and in order to identify the bands she worked with mixtures of the various solvents, so as to get what she supposed was a gradual shift of the bands. Her plates, however, show that instead of having a shift in the bands, she had two sets of bands existing simultaneously.

In the second part of her investigation she studied change in absorption with change in concentration; in other words, whether Beer's law held. She found that with decreasing concentration there is a shift in the yellow band towards the violet. The most concentrated solutions with which she worked contained about 30.5 grams of didymium nitrate in 10 cc. water. She concludes that all of the facts established by her investigation can be accounted for in terms of electrolytic dissociation alone.

An excellent piece of work on the absorption spectra of aqueous solutions of neodymium chloride has recently been done by Rech.[1] The absorption bands were carefully measured as far down into the red as the sensibility of his plates would permit. There is transmission farther down into the red than could be detected by the plates which he employed.

The absorption spectra of a number of the powdered salts of neodymium and erbium were recently studied by Anderson.[2] These included the chloride, nitrate, sulphate, and oxalate. He found that each salt has its own definite absorption, which is different from that shown by any other salt.

Preparation of Anhydrous Salts.

In working in nonaqueous solvents, it is, of course, necessary to have the dissolved salts perfectly anhydrous. A number of the salts used in this investigation cannot be dried in the air by simply raising the temperature. Under these

[1] Dissertation, Bonn, 1906.
[2] Astro-Phys. Rev., **26**, 73 (1907).

conditions the oxy salt would be formed. This applies to most of the chlorides and bromides whose nonaqueous solutions were studied in this work.

In every such case the chloride in question was dried in a current of dry hydrochloric acid gas. It was placed in a porcelain boat, which was then inserted into a glass tube through which the current of dry hydrochloric acid gas was passed. The glass tube was then heated in an air bath to the temperature required to remove all of the water from the salt.

In removing all of the water from a bromide, the salt was treated in every respect like the chloride, except that it was dried in a current of dry hydrobromic acid gas. The usual methods of testing the purity of all of the compounds employed, and of standardizing the mother solutions of these substances, were used. A detailed discussion of this subject would be superfluous.

The praseodymium and neodymium, in the form of the double nitrate with ammonium, were furnished us by the Welsbach Light Company, with their characteristic generosity, and it gives us unusual pleasure to express here our heartiest thanks to their chemist, Dr. H. S. Miner. The chemists of this company have always shown a spirit of coöperation with scientific work on the rare elements that is very unusual, and for which men of science, working in this field, owe them a lasting debt of gratitude.

The praseodymium used in this work was practically free from neodymium, containing only a few hundredths of 1 per cent of that element. From the spectrograms it would appear that the neodymium used contained about 6 per cent of praseodymium. The erbium, of course, contained quite a considerable amount of impurities.

A number of the salts of neodymium, praseodymium, and erbium were studied thoroughly in the present connection, and yielded some of the most interesting and important results obtained in this investigation.

Thus, plates were prepared for: Neodymium chloride in water—Beer's law; neodymium chloride in water—molecules constant; neodymium chloride in water with calcium chloride

and with aluminium chloride; neodymium chloride in methyl alcohol—Beer's law; neodymium chloride in ethyl alcohol—Beer's law; neodymium chloride in mixtures of methyl alcohol and water; neodymium chloride in ethyl alcohol to which water is added; neodymium chloride —anhydrous; neodymium bromide in water—Beer's law; neodymium nitrate in water—Beer's law; neodymium nitrate in water—molecules constant; neodymium nitrate in methyl alcohol—Beer's law; neodymium nitrate in ethyl alcohol—Beer's law; neodymium nitrate in acetone—Beer's law; neodymium nitrate in mixtures of methyl alcohol and water; neodymium nitrate in mixtures of acetone and water; praseodymium chloride in water—Beer's law; praseodymium chloride in mixtures of the alcohols and water; praseodymium nitrate in water—Beer's law; erbium chloride in water—Beer's law; erbium nitrate in water—Beer's law.

On account of the relative importance of the results in this section of our work, fifteen plates for the salts of the rare earths are given.

Neodymium Chloride in Water—Beer's Law (*See Plates XI. and XII.*).

Five different sets of solutions, covering as wide a range of concentrations as possible, were made up, the object being not only to test Beer's law thoroughly, but also to get as complete a map as possible of the absorption spectrum of neodymium chloride. In very concentrated solutions a certain group of bands may appear as a single band, due to the widening of the individual band or to general absorption in the region considered. By diminishing the concentration such a "band" breaks up gradually into its components, and hence to map completely the absorption spectrum it is necessary to work over a wide range of concentrations.

If the object were simply to "map the spectrum" this could, of course, be most conveniently done by keeping the depth of layer constant and changing the concentration through a sufficient range, thus getting the complete spectrum on a single film; but since the chief object here was to test Beer's

law it was necessary to make several sets of solutions covering different regions of concentration. The concentrations of the solutions used in making the negative for A, Plate XI., beginning with the one whose spectrum is adjacent to the numbered scale, were 3.40, 3.02, 2.72, 2.38, 2.17, 1.90, and 1.70; the corresponding depths of cell were 12, 13.5, 15, 17, 19, 21.5, and 24 mm. For B, Plate XI., the concentrations were 3.40, 2.55, 1.70, 1.13, 0.80, 0.57, and 0.43; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For A, Plate XII., the concentrations were 1.70, 1.27, 0.85, 0.57, 0.40, 0.28, and 0.22; for B, Plate XII., they were 0.85, 0.63, 0.42, 0.28, 0.20, 0.14, and 0.11. The depths of absorbing layer were in each case the same as in B, Plate XI. It will be noticed that beginning with B, Plate XI., the concentrations used in each succeeding set are just halved each time.

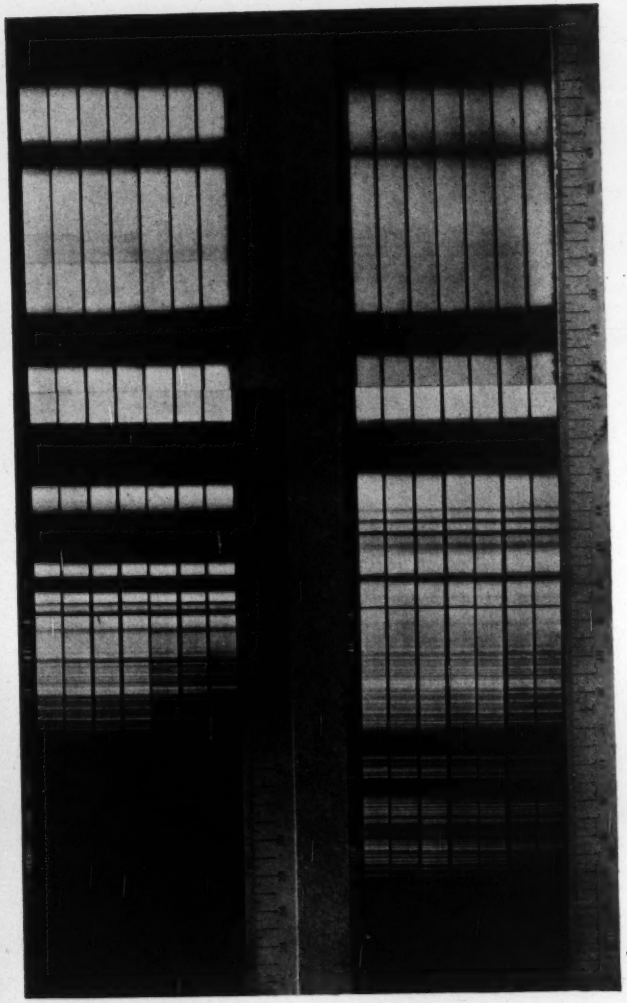
The most concentrated solutions appeared brownish-yellow in their bottles, and changed on dilution to a yellowish-pink, the color being extremely faint in the most dilute solutions.

The exposures to the light of the Nernst lamp and spark were 1 and 2 minutes, respectively, the slit having a width of 0.01 cm. The exposures and slit width were not varied in the work recorded in the present section, the object being to make the spectrograms as nearly comparable as possible.

Both A and B, of Plate XI., show the presence of some general absorption in the ultraviolet, which decreases quite rapidly with dilution. The absorption bands also narrow somewhat with decrease in concentration, especially from 3.4 normal to about 1.7 normal. For concentrations less than about 1.5 normal Beer's law seems to hold very accurately indeed, with the exception of the shading towards the red accompanying the band near λ 5800, which seems to decrease somewhat with dilution for concentrations of normal or less.

In the following table the measurements of the positions of the bands were made on the seventh strip of A, Plate XI., and refer, therefore, to a concentration of 1.7 normal with a

Plate XI.



A B

depth of layer of 24 mm. The remarks referring to changes with dilution apply to a change in concentration from 3.4 to 1.7 normal, the depths of layer being so varied that the product of concentration and depth remains constant.

λ.	Character.	Remarks.
2810	Faint transmission begins	
2890–2910	Band with well-defined sharp edges	
2970–2995	A double band, strongest component to violet	The observed narrowing with dilution perhaps due largely to general U.V. absorption
3220–3330	Strong band of complete absorption, sharp edges	Narrows slightly with dilution
3380–3400	Rather faint band. Most intense towards red	
3435–3595	Complete absorption. Edges sharp	
4180	Hazy, not very intense	Narrows somewhat with dilution
4275	Very intense and sharp	Narrows considerably at first
4290	Narrow and faint	Between this and λ 4275 there is fairly strong absorption in the most concentrated solution. This absorption has disappeared in the spectrum measured
4330	Hazy	
4410–4465	Edges rather hazy	This band is coincident with band due to praseodymium, and is to be ascribed to this element, which had not been completely separated from the neodymium. It does not change with dilution
4580–4650	Band with hazy edges, not completely separated from 4665–4710	Narrows slightly with dilution
4665–4710	More sharply defined on red than on violet side	Partly due to praseodymium Does not change with dilution

λ	Character.	Remarks.
4740–4770	Fairly sharp edges	Not affected by dilution
4820	Hazy on violet side	Due at least partly to praseodymium
5000–5330	Red limit sharp, violet a little hazy	Violet shading a little greater in concentrated solutions
5660–5930	Violet limit sharp. Red edge hazy	Shading on red side decreases with dilution
6235	First and strongest band in orange group	Not affected by dilution
6260	Narrow and rather faint	"
6270–6310	Faint band	"
6300–6390	"	"
6730	Faint. In shading of principal red band	"
6770–6840	Principal red band. Edges hazy	"
6890	Band with hazy edges	"
7250	End of transmission	"

The most marked change produced by dilution from 3.4 to 1.7 normal, excepting that in the red shading of the λ 5660 to λ 5930 band, is that which takes place on the red side of the narrow absorption line at λ 4275. In the spectrum of the most concentrated solution the red edge of this line falls at λ 4280, from which a uniform absorption extends to λ 4295. In the third spectrum, counting from the numbered scale, the shading has almost completely disappeared, leaving a very narrow line at approximately λ 4290. The width of this line is only 2 or 3 A.U., and it persists with unchanged intensity throughout the remaining strips of the spectrogram. Its intensity is, however, not sufficient to make it show in the reproduction, and not even great enough to make it visible on the negative for B, Plate XI.

The limits of transmission for the yellow band, as shown by the spectrum of the most concentrated solution, are λ 5660 and λ 5950; hence the narrowing of its red side amounts to 20 A.U.

B, Plate XI., starts at the same concentration as A, but the effective depth of absorbing layer is only one-fourth of

Plate XII.

A B

that used in A. Hence this spectrogram represents the spectrum of a solution of neodymium chloride 24 mm. deep and having a concentration of 0.43 normal. The absorption bands are all much narrower, and several of them are shown in the process of breaking up into simpler bands. The bands in the ultraviolet have disappeared, excepting the one at λ 3435 to λ 3595, which is still intense, and a trace of the one at λ 3220 to λ 3330. Transmission in this region now extends faintly to λ 2460. No new absorption bands beyond λ 2800 can be seen.

The λ 3435 to λ 3595 band now has the limits λ 3450 to λ 3580, and shows a weak transmission at λ 3485, which increases somewhat with dilution, the band thus being divided into two. In A, Plate XII., this has broken up further into bands having their centers at λ 3465, λ 3500, λ 3540, and λ 3560, the bands at λ 3465 and λ 3540 being the narrowest and most intense. In B, Plate XII., λ 3465 and λ 3540 are both narrow, intense bands, while λ 3500 is faint and wide; λ 3560 has disappeared entirely as a band.

The band at λ 4180 is weak throughout B, Plate XI., and may be said to have disappeared in A, Plate XII. The narrow band at λ 4275 is very persistent. Its width remains about the same as that shown by the negative for B, Plate XI., throughout the range of concentrations studied. The band at λ 4330 behaves exactly like the one at λ 4180, practically disappearing in A, Plate XII.

The band having its middle at λ 4445 is perhaps due entirely to the praseodymium present as an impurity. In A, Plate XI., it has about the same intensity as in a solution of praseodymium chloride having a concentration of 0.85 and a depth of absorbing layer of 3 mm. This indicates that the proportion of praseodymium in the neodymium salts used was about 6 per cent. The band at λ 4825, partly due to praseodymium, may also be seen throughout the entire series under consideration. Since the wave length of the praseodymium band is λ 4815, it is seen that neodymium has a band nearly coincident with that given by praseodymium, but lying a little closer to the red end of the spectrum.

The remaining praseodymium band has the position λ 4685, thus nearly coinciding with the rather narrow, strong neodymium band whose position is λ 4695.

The band which under A, Plate XI., was recorded as having the limits λ 4580 to λ 4650 shows in B as a hazy band with its center at λ 4615, together with a narrow, faint line at λ 4645. The band is visible in A, Plate XII., but has practically disappeared from view in B, of the same plate. The narrow line at λ 4645 does not show beyond B, Plate XI.

The band which in the table is recorded as λ 4740 to 4770 has in B, Plate XI., become a slightly hazy band having its middle at λ 4760. Its intensity is intermediate between that of the bands at λ 4695 and λ 4825, and hence like them may be seen faintly even in the plate corresponding to a dilute solution.

The band which in A, Plate XI., has the limits λ 5000 to λ 5330 breaks up on dilution into a rather complicated series of bands, some idea of which may perhaps be gained from the following: B, Plate XI., shows some absorption throughout the region given, but with a deep, narrow band at λ 5090 and faint transmission at λ 5100 and in the region λ 5150 to λ 5180. Absorption is complete from λ 5105 to λ 5150, and from λ 5180 to λ 5270. There is again incomplete absorption from λ 5270 to λ 5330, with indication of a band at λ 5315. In A, Plate XII., the general shading has the limits λ 5050 to λ 5330, and it shows the following: A narrow intense band at λ 5090; wide, hazy band at λ 5125; a pair of very intense, narrow bands at λ 5205 and λ 5222; very narrow band at λ 5255; and faint, hazy band at λ 5315. B, Plate XII., shows the shading diminished very much in intensity, and all the bands except the doublet λ 5205 to λ 5222 rather faint. The absorption in the doublet is still almost complete.

The limits of the yellow band in B, Plate XI., are λ 5700 to λ 5880 in the strip corresponding to the most concentrated solution. The band narrows by 30 Angström units on this spectrogram, the narrowing being due to a decrease in the shading towards the red, with decrease in concentration.

In B, Plate XII., the limits of the band are λ 5710 and λ 5840. There is still considerable shading, but it decreases only very slightly with dilution. The band begins to show its structure, but not well enough to allow any measurements to be made.

In B, Plate XII., the band has broken up into the following smaller bands: λ 5725, narrow and moderately intense; λ 5745 and λ 5765, double band, not clearly resolved, the red component being more intense than the violet. This double band is the most intense of the group. λ 5795, band having about the same intensity as the one at λ 5725, but being much wider and hazier; λ 5380, very faint band.

The group of absorption bands in the orange, given in the table, may be seen faintly in B, Plate XI., and very faintly in A, Plate XII., but, like the group in the red near λ 6800, it shows no further breaking up into more complicated bands on dilution.

B, Plate XI., shows that the spectrum ends at λ 7310 in what appears to be an absorption band. In Plate XII., it is seen that there is a very intense, narrow band at λ 7325; another narrow but fainter band at about λ 7350; and a wide, moderately intense band at λ 7390 or λ 7400, beyond which the plates were not sufficiently sensitive to give any appreciable photographic action with the length of exposure used.

The most intense bands of neodymium chloride, and hence the ones that would be most conspicuous in a very dilute solution, are the following: λ 3465, λ 3540, λ 4275, λ 5205, λ 5225, λ 5745, λ 5765, and λ 7325.

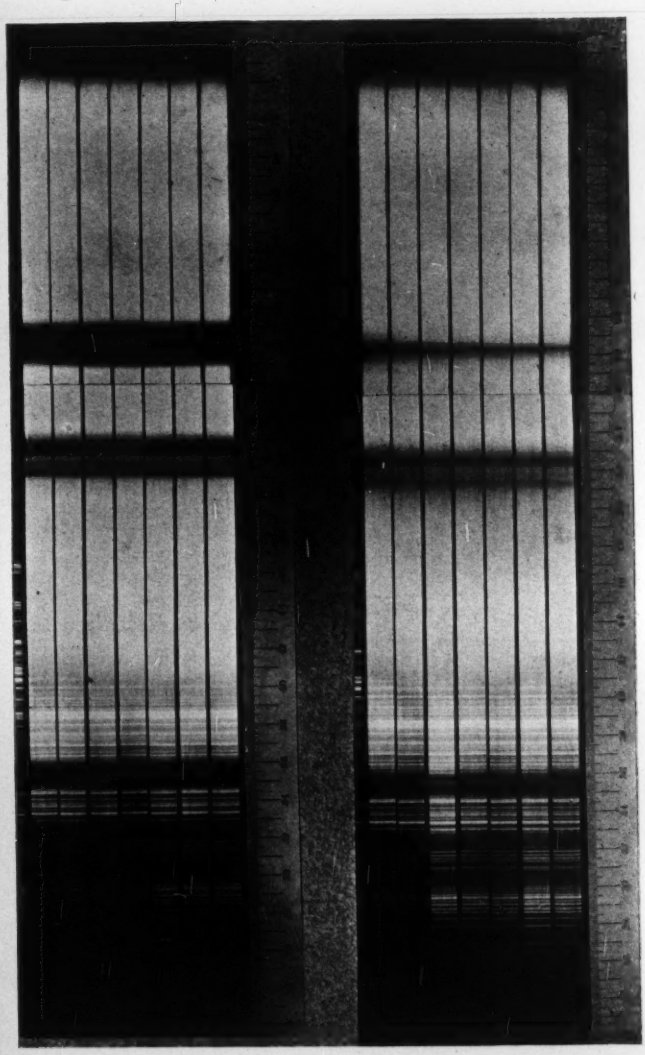
The wave lengths of all the bands, together with a brief description of the appearance of each band, are collected in the following table. It is to be understood that this table is not meant to represent what could be seen or photographed in any one solution of neodymium chloride in water. It merely records the position of all the bands which can be seen in a layer from 3 to 12 mm. deep, when the concentration is varied from 0 to 3.4 normal.

λ.	Character.
2900	About 20 A.U. wide
2985	About 25 A.U. wide
3225	Narrow and sharp
3390	Narrow, faint
3465	Very intense, narrow
3505	Rather wide
3540	Very intense, narrow
3560	Faint, narrow
4180	Faint, hazy
4275	Very intense and sharp
4290	Very narrow, faint
4330	Hazy edges
4615	Rather wide and hazy
4645	Very narrow, faint
4695	Narrow, intense
4760	Hazy edges, fairly narrow
4825	Narrow and fairly intense
5090	Narrow, intense
5125	Rather wide and hazy
5205	Very intense, narrow
5222	"
5255	Narrow, intense
5315	Hazy edges, faint
5725	Narrow, intense
5745	Very intense
5765	"
5795	Intense, moderately narrow
5830	Very faint and hazy
6235	Fairly narrow
6260	Very narrow, faint
6270–6310	Faint, hazy edges
6360–6390	"
6730	Faint band
6800	Moderately intense, hazy edges
6890	Hazy edges
7325	Very intense and narrow
7390	Rather wide band

Neodymium Chloride in Methyl Alcohol—Beer's Law (*See Plate XIII.*).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.50, 0.40, 0.315, 0.25,

Plate XIII.



A B

0.20, 0.16, and 0.125; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm. The concentrations for B were, in the same order, 0.20, 0.16, 0.13, 0.10, 0.08, 0.06, and 0.05; the depths of cell were the same as used in A.

There is some absorption in the extreme ultraviolet, which, however, is to be ascribed to the solvent and not to the neodymium chloride.

No trace of absorption due to the dissolved substance is visible until we reach the group of bands near λ 3500. There are three bands having their centers at λ 3475, λ 3505, and λ 3560. Of these the one at λ 3560 is the widest and also the most intense, while the one at λ 3475 is somewhat fainter than that at λ 3505. The bands are all much wider and hazier than those occurring near the same place in the aqueous solution. No change with dilution indicating a deviation from Beer's law can be detected in these or any of the other bands in the alcoholic solutions of the chloride.

In the violet and blue regions we find the following: A band at λ 4290, about 10 A.U. wide and only moderately intense. At λ 4325, a band somewhat wider and fainter. At λ 4460, a rather wide hazy band with a faint hazy companion towards the violet. This is the band which is perhaps due to praseodymium. The much greater concentration of the alcoholic solutions of praseodymium chloride studied in this work makes it impossible to verify this, by seeing whether the praseodymium band in dilute solution really has this general character.

There are bands at λ 4700, λ 4780, and λ 4825, all of about the same intensity, the one at λ 4770 being, however, much narrower than the other two, of which λ 4825 is somewhat the wider. Both λ 4700 and λ 4780 have faint companions towards the violet.

The group in the green is made up of six bands as follows: λ 5125, hazy and rather wide, moderately intense; 5180, also hazy but much fainter; λ 5220, moderately intense and narrow; λ 5245, intense, and with faint companion towards

the red; λ 5290, narrow and moderately intense, shading as far as λ 5330, with indications of a faint band at λ 5315.

The yellow group is made up of seven bands having the following characteristics: λ 5727, moderately intense with hazy edges; λ 5765, narrower, but not quite as intense as λ 5725; λ 5800, fairly narrow, strong; λ 5835, very intense; λ 5860, hazy and moderately intense, not clearly separated from λ 5835, shading to λ 5970, with two faint bands superimposed upon it, one at λ 5895 and the other at λ 5925.

No trace of bands is to be seen in the orange, but in the red there is a fairly narrow but faint band at λ 6860. The spectrum ends at λ 7355 in a deep, rather narrow band. It is evident that the spectrum of neodymium chloride when dissolved in methyl alcohol is quite different from its spectrum in aqueous solution, but this point will be taken up more fully in the discussion of Plates XV. and XVI.

Neodymium Chloride in Ethyl Alcohol—Beer's Law (*See Plate XIV.*).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.50, 0.40, 0.315, 0.25, 0.20, 0.16, and 0.125; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm. For B, the concentrations were 0.20, 0.16, 0.13, 0.10, 0.08, 0.06, and 0.05; the depths of cell were the same as those used in A. The concentrations and depths of cell were, therefore, exactly the same as those in methyl alcohol, so that Plates XIII. and XIV. are directly comparable. A very careful comparison of the two plates reveals the remarkable fact that the two spectra are practically identical, the very slight differences noted being perhaps due to slight differences in development of the negatives.

In view of the great difference between either one of these spectra and that of the aqueous solution, this similarity is rather surprising, and it led us to think that perhaps in these alcoholic solutions we were getting the absorption of the neodymium chloride molecules themselves, while in the aqueous

A B

solution we get the absorption of some compound of the molecules with water. But that this is not the case was shown by the spectrum of anhydrous neodymium chloride (Plate XVII.), which is very different from that of any of the solutions. The spectrum of the alcoholic solutions is, therefore, not that of the $NdCl_3$ molecule *per se*, but must be that of some solvate of it or of the neodymium ion. But that solvates with methyl alcohol and ethyl alcohol should affect the frequencies of the vibrators in the metallic atom so very nearly in the same way seems a little surprising, to say the least, especially as solutions of the nitrate in the two solvents give somewhat different spectra, as will be fully discussed when we come to consider Plates XXI. and XXII.

The very slight differences between the bands shown in Plates XIII. and XIV. seemed to indicate that they were a little more hazy in the ethyl alcohol solutions, but the development of the negatives for Plate XIV. was not carried quite as far as was the case with those for Plate XIII., and this would tend to produce just the kind of difference that was noted.

Neodymium Chloride in Mixtures of Methyl Alcohol and Water (See Plates XV. and XVI.).

Since, as we have just seen, the absorption spectrum of neodymium chloride in aqueous solution is so different from that of the alcoholic solutions, it was thought to be of some interest to see how the change from one to the other would take place if one of the solvents was made to displace the other gradually. A series of solutions was accordingly made up, the concentration of the dissolved salt being constant and equal to 0.5 normal, but the character of the solvent varied as follows: The percentages of water in the seven solutions were 0, 16.6, 33.3, 50, 66.6, 83.3, and 100; the corresponding percentages of methyl alcohol were 100, 83.3, 66.6, 50, 33.3, 16.6, and 0. Two spectrograms were made, namely, A, Plate XV., where the depth of the cell was 1.5 cm., and B, where the cell had a depth of only 5 mm. A was made in order to show clearly the change taking place in the narrower

and fainter bands, while B was intended to show the change of structure of the more intense bands, such as the green and yellow ones. The strip which is adjacent to the numbered scale belongs to the solution in pure water, while the one nearest the narrow, comparison spark spectrum belongs to the solution in pure methyl alcohol.

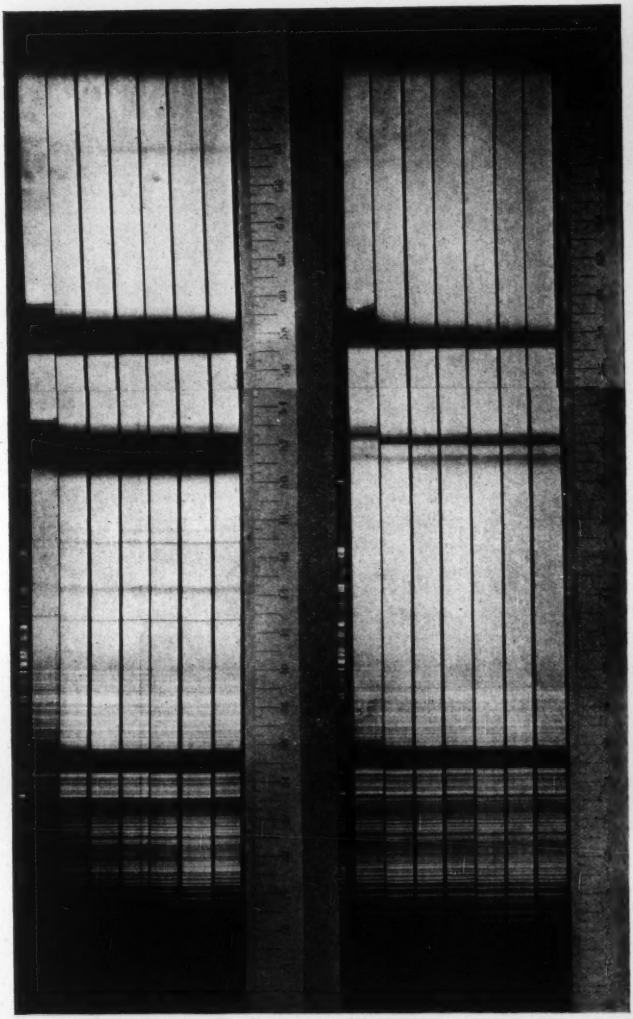
Plate XV. shows that, beginning with the strip nearest the scale, the first six spectra are very nearly identical. From the sixth to the seventh there is an abrupt change, which at first sight consists in a shift of all the bands towards the red, but which on closer examination is seen really to consist in a disappearance of one spectrum and the appearance of the other. Since the first strip is the spectrum of the solution in pure water, and the sixth is nearly identical with the first, it follows that as large a proportion of alcohol as 83 per cent in the solvent does not change the absorption spectrum materially; the chief change takes place when the percentage of alcohol is varied from 83 per cent to 100 per cent.

It is to be noted that the apparent shift of the bands towards the red is in reality not quite as great as it appears to be at first sight from Plate XV., owing to the fact that the film accidentally shifted slightly towards the red between the sixth and seventh exposures. The amount of this mechanical shift is easily seen, however, by comparing the spark lines in the ultraviolet. A measurement of the shift shows that it is approximately 3 Angström units, and the same for both A and B, while the "apparent" shift of the absorption line at λ 4275 in aqueous solution is actually 15 Angström units, its position in the alcoholic solution being 4290.

The slight changes taking place in some of the bands throughout the spectrograms of Plate XV. are perhaps sufficiently clear in the reproductions. However, as a good deal of the detail shown by the negatives is lost even in the most perfect processes of reproduction, we give here a description of the changes taking place in two of the bands as seen on the original negative. We select the bands at λ 4275 and λ 4760 from the negative for A, Plate XV.

In the aqueous solution the λ 4275 band is very intense

Plate XV.



A B

and narrow, its whole width being less than 5 Angström units. The edges are only very slightly shaded. In the alcoholic solution the position of the center of the corresponding band is λ 4290. It has a width of from 12 to 13 Angström units, and is not nearly as intense as in the aqueous solution.

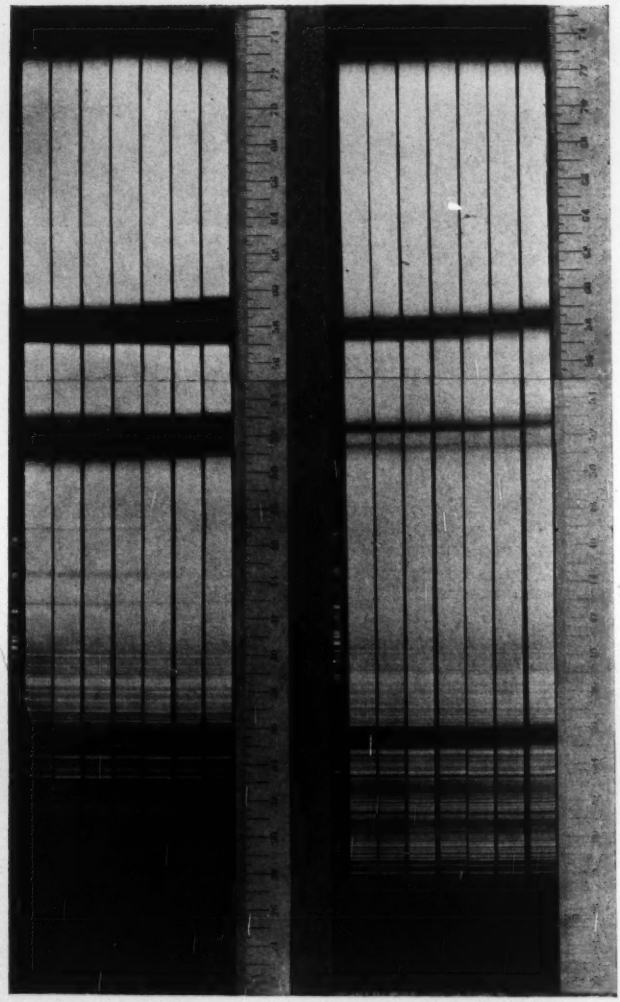
Throughout the first six strips the λ 4275 band maintains its position and intensity almost unchanged. Its position does not change in the least, but its intensity in the sixth strip is a trifle less than in the others. In the seventh strip there is not the faintest trace of it left. In the third strip, corresponding to the solution whose alcohol content was 33.3 per cent, there appears at λ 4285 an extremely faint and narrow line. In the fourth strip it is somewhat wider and more intense, but its center is still at λ 4285. In the fifth strip it is beginning to be fairly conspicuous, and in the sixth it is a band of moderate intensity, having its center at about λ 4287. This band is undoubtedly the same one which in the pure alcoholic solution has its center at λ 4290 or very near there, the exact wave length being perhaps nearer to λ 4292. We see, then, that even when the mixed solvent contains only about one-half alcohol, this band exists independently of and distinct from the band characteristic of the aqueous solution; that it is at first only a very narrow and faint line, which widens towards the red as the percentage of alcohol is increased.

The band whose center is at λ 4760 has the following appearance in the aqueous solution: Faint absorption begins at λ 4748 and rises rapidly to a maximum between λ 4755 and λ 4760, then decreases slowly to nothing at λ 4775. The band is accordingly a trifle asymmetrical, the slope towards the violet being considerably steeper than that towards the red. The corresponding band in the alcoholic solution is double and answers the following description: Very faint absorption begins at λ 4753, and rises to a faint maximum at about λ 4757, becoming again zero at λ 4760. It begins again at λ 4772, rises rapidly to a strong maximum at λ 4780, and falls to zero at λ 4790. The component whose center is at λ 4757 is very faint compared with the main band.

In the first and second strips we have nothing but the band corresponding to the aqueous solution. In the third strip the red side of the band has increased slightly in intensity, making it appear much more nearly symmetrical. This change increases in the fourth and fifth strips, the band at the same time widening considerably. In the sixth strip its appearance is as follows: Absorption begins at λ 4748 and rises to a maximum just to the violet side of λ 4760, then decreases slightly towards λ 4770, after which it increases somewhat to λ 4778, then falls off to zero at λ 4787. It is very evident from a study of the change in this band that the two bands characteristic of the aqueous and alcoholic solutions coexist, and that the band appearing in our photographic strip is the sum of the two taken in different proportions, the proportion of the alcohol band being, however, very much smaller than the proportion of alcohol in the corresponding solution. A similar description might be given for any one of the other bands, but this is not necessary, as the changes are of exactly the same nature as those we have already indicated. In every case where the alcoholic solution has a strong band which differs somewhat in position from any band in the aqueous solution, we begin to see traces of this band when the proportion of alcohol in the mixture reaches 50 per cent; but the band remains comparatively faint even when the proportion is as high as 83.3 per cent.

In order to study more carefully the change which takes place between the sixth and seventh strips of the spectrograms of Plate XV., a series of alcoholic solutions was prepared containing the following percentages of water: 0, 2.6, 5.3, 8, 10.6, 13.3 and 16. The concentration of the neodymium chloride was constant and equal to 0.5 normal. Two spectrograms were made, one with a depth of absorbing layer of 1.5 cm. in order to show the fainter bands, and the other with the depth of the cell of only 5 mm. in order to show as much as possible of the structure of the larger bands. The first spectrogram is reproduced in Plate XVI., A, and the second in Plate XVI., B. The strips corresponding to the pure alcohol solutions are adjacent to the numbered scale, the spec-

Plate XVI.



A B

trum of the solution containing 16 per cent water being next to the comparison spark spectrum.

Although we found, in considering Plate XV., that some slight change in the spectrum takes place when the percentage of alcohol is changed from 0 to 83 per cent, yet this change is so small, and the bands due to the aqueous solution are so strong, that we may regard the spectrum of a solution containing 16 per cent of water as practically that of the aqueous solution. Accordingly, the spectrograms on Plate XVI. may be taken to show very nearly the whole change which takes place when the solvent of neodymium chloride is gradually changed from pure water to pure methyl alcohol.

In A the ultra violet is rather too intense to allow its structure to be seen. Accordingly, we see the whole band remain sensibly unchanged as the water is varied from 16 per cent to 8 per cent, and it shifts towards the red with increasing rapidity as the water is reduced to zero, the whole apparent shift amounting to about 20 Angström units. On the negative the intense band at λ 3465 may be clearly seen, however, and its intensity decreases very slowly from the first to the third strips, counting from the narrow, comparison spark spectrum. In the fourth strip its intensity is about half of what it was in the first strip, and from this it decreases rapidly, vanishing entirely in the strip nearest the scale.

In B the structure of this band is seen very distinctly, and we find that the bands characteristic of the aqueous solution gradually decrease in intensity, especially from the third to the fourth strips, while the wider bands, characteristic of the alcoholic solutions, increase in intensity, the two sets existing together. The change in the band at λ 4275 is the one that shows the best, because here the two bands belonging to the aqueous and alcoholic solutions, respectively, are both intense and narrow and clearly separated from one another.

The alcoholic band is clearly visible in the first strip, and it increases continuously in intensity as the amount of water is decreased, but more rapidly from the fourth to the seventh strips than from the first to the fourth. Its position also

shifts somewhat towards the red from the first to the fourth strips, the wave lengths of its center for the two strips being λ 4287 and λ 4292, respectively. Accompanying this shift is a change in its character, which may be made clear by the following statements: In the first strip it has the appearance of an unsymmetrical band, the maximum intensity being nearer the violet. In the third strip it extends from λ 4280 to λ 4295, and has about the same intensity throughout. In the fourth strip the intensity of its violet edge has decreased while that of the red edge has increased considerably, giving the band an unsymmetrical appearance, with the maximum intensity towards the red. In the fifth strip the violet shading from λ 4280 to about λ 4284 has disappeared, leaving a band very nearly symmetrical about λ 4290. It appears, therefore, that we are really dealing with two unresolved bands, one having its center at about λ 4285 and the other at λ 4292.

The band at λ 4275, due to the aqueous solution, decreases in intensity throughout, but more rapidly from the third to the sixth strips than at first. Its position remains the same throughout. As near as the eye can judge the intensity of this band is reduced to about half-value when the fourth strip, corresponding to 8 per cent of water in the solution, is reached. The alcohol band at λ 4292 also has about 50 per cent of its final intensity in the same solution.

The band at λ 4760 shows the same kind of a change that we described in some detail above, only here the change is much more gradual and easy to follow. It also shows about equal intensity for the two sets of bands when the amount of water is 8 per cent of the whole

The green and yellow bands are not sufficiently resolved in A to allow the change in the individual bands to be followed, and hence these apparently show only a gradual shift towards the red with decrease in the amount of water. In B, however, they are both sufficiently resolved to enable us to follow the change in each individual band, although this is a little difficult in some cases on account of the large number and the incompleteness of separation of the bands. The

change is in every respect the same as we have found for the other bands, namely, the bands due to the aqueous solution diminish in intensity, and reach about half-value in the 8 per cent water solution, while those belonging to the alcoholic solution increase in intensity as the amount of water is decreased.

The band in the red near λ 6800 shows the change very well indeed, the "water" band having the position λ 6800, while that pertaining to the alcoholic solution is situated at λ 6860, and hence the two are well separated. Here the point of equal intensity appears to be reached in the solution containing 10.6 per cent of water, but this is due to the fact that the alcoholic band has a considerably greater intensity than that of the aqueous solution, the conditions as to concentration and depth of layer being the same. Taking this into account, it is seen that this band obeys substantially the same rule as the others.

The change in the band at λ 7325 is more difficult to follow on account of the small intensity of the photographic action on the less refrangible side of this position. The band belonging to the aqueous solution may be seen very clearly even in the strip corresponding to the 2.6 per cent water solution, but is, of course, entirely absent in the alcoholic solution. Its intensity in the 2 per cent solution, however, seems a little greater than we should expect from the behavior of the other bands, but this is perhaps due to the rather weak photographic action in this part of the spectrum, combined with the great intrinsic intensity of the band. The alcoholic solution transmits light as far as λ 7355, where its spectrum ends abruptly in a band.

Throughout this description we have laid great stress on the fact that on Plate XVI. the two sets of bands coexist, the bands due to the aqueous solution decreasing, while those belonging to the alcoholic solution increase in intensity with decrease in the percentage of water; we have also called attention to the fact that the two sets of bands have about half their full intensity in a solution containing about 8 per cent of water. This was for a 0.5 normal solution.

The next question which suggested itself was whether the composition of the solvent which gives the two sets of bands with about half their normal intensity is independent of the concentration of the dissolved substance. If this were the case, then we should have to conclude that the determining factor is the nature of the solvent; while if the requisite composition of the solvent depends upon the concentration the ratio between the amount of dissolved substance and one or other of the solvents would perhaps be the important thing. To answer this question a set of solutions was made up in which the solvent was kept exactly the same as it was for the solutions used in making the negatives for Plate XVI., but the concentration of neodymium chloride was made 0.25 normal instead of 0.5 normal. In order to have this spectrogram directly comparable with B, Plate XVI., the depth of cell was kept at 1.0 cm. throughout.

A study of the negative showed that the two sets of bands have about half their normal intensity in the third strip, counting from the numbered scale, corresponding to 5.3 per cent of water. In the fourth strip the bands characteristic of the alcoholic solutions are very weak compared with the bands belonging to the aqueous solution, while in the second strip the opposite is the case. It is plain, therefore, that the composition of the solvent which gives the two sets of bands with about half their normal intensity depends upon the concentration, and it also seems very probable that, provided the ratio of water to dissolved substance is kept constant, the two sets of bands will not vary much in relative intensity. A simple calculation shows that in the solutions which produced the bands with about half their normal intensity, there were present approximately 10 molecules of water to 1 molecule of neodymium chloride.

Neodymium Chloride—Anhydrous (*See Plate XVII.*).

This plate was made in order to see whether the spectrum of the anhydrous salt is identical with that observed when the salt is dissolved in pure methyl or ethyl alcohol. The anhydrous salt was in the form of a very fine powder and was con-

tained in a bottle with a tight-fitting glass stopper. An image of the Nernst filament was thrown on the surface of the powder in contact with the walls of the bottle, and this image was in turn focussed on the slit of the spectroscope by means of the concave spectrum mirror. The light falling on the grating was necessarily very faint, therefore rather long exposures were necessary; but this caused no inconvenience, since the Nernst lamp burns so steadily that it needed no attention whatever. In order to show as well as possible both the strong and the weak bands, a series of exposures was made on the same film, the times of exposure, beginning with the strip nearest the numbered scale, being 30 minutes, 1 hour, 1.5 hours, 2 hours, and 2.5 hours. On account of the fact that the beam of light had to pass through the glass condensing lenses, as well as the glass walls of the containing bottle, the spectrum ends at about λ 3450 for the strip nearest the comparison spectrum, and at λ 3600 for the one nearest the scale.

The comparison spark spectrum in this case was made by using zinc terminals instead of the carbon terminals employed throughout the rest of the work. Since there is usually some accidental shift between the successive strips on a film, and since no light but that of the Nernst filament was used in making the five strips on Plate XVII., it is evident that no accurate wave length measurements could be made by a comparison with the spark spectrum on this plate. In fact, the position of a given absorption line, which appeared both on the film and on the red-sensitive plate, was found to differ by as much as 10 Angström units as measured from the two negatives. Hence it was necessary to determine the position of one or more of the absorption lines by comparison with a spark spectrum which had been impressed on the plate without moving this between the exposures to the light reflected from the chloride powder and to that from the zinc spark. This was accomplished by making an exposure of about an hour for the absorption spectrum and then, without moving the plate holder, impressing the ultraviolet portion of the spark spectrum on the same strip. Thus, the positions of a

few of the strongest and sharpest absorption bands are determined, and the positions of the others were measured by determining their distances from the standards.

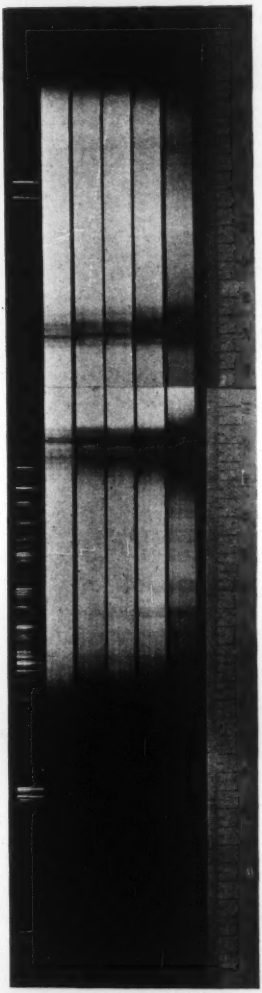
On the whole, the spectrum is similar to that observed in solutions; that is, if the solutions show a group of absorption bands in a certain region, then there is also a group of bands in nearly the same place in the spectrum of the light reflected from the anhydrous salt; but as a rule, the individual bands in the group are much narrower and more numerous in the latter than in the former. This agrees with what has previously been found by Becquerel[1] and by one of us.[2]

In the following table, the position and character of the stronger bands are given. No attention was paid to the numerous bands which are so faint as to require special precautions in order to set on them, as the object of the present work was not so much to catalogue the spectra as to try to get some idea as to the causes of the changes which take place when the substance is subjected to different conditions.

λ.	Character.
3500	Rather strong, narrow band
3537	Weaker and wider
3570	Narrow and intense
3595	Narrow and very intense
3612	Rather faint and hazy
4045	Weak and hazy. Perhaps 2 or 3 bands
4080	More intense, but hazy
4210	Faint, narrow
4228	Faint, perhaps 2 bands
4308	Very narrow and intense
4313	"
4333	Wider and a little hazy, but intense
4357	Narrow, shaded towards red
4455	Wide and hazy
4500	"
4640	Faint, hazy
4680	Faint, hazy
4717	Narrow and moderately intense
4725	"
4735	"

[1] H. Becquerel: Ann. Chim. Phys. [6], **14**, pp. 257 *et seq.*
[2] J. A. Anderson: Astro-Phys., J., **26**, pp. 73-94 (1907).

[Plate XVII.



λ.	Character.
4775–4790	Sharp on violet side, perhaps 2 bands
4815	Rather narrow
4855	Intense and narrow
4872	Weak
4888	Narrow, and moderately intense
4895	"
5000–5370	Strong general absorption
5088	Weak, slightly hazy
5117	Stronger, shaded somewhat
5147	Narrow, intense, hazy on violet edge
5174	Intense, slightly hazy
5183	Not as narrow as 5174
5216	Shaded to violet
5254	Very intense and narrow
5267	"
5282	Weaker and wider than the last two
5300	Shaded towards red, perhaps double
5328	Intense, narrow
5342	Weaker and broader
5760–6000	Strong general absorption
5768–5782	Very intense, double band
5807	Narrow and intense
5829	Most intense band in spectrum
5858	Very narrow
5875	A little hazy
5890	Weak
5902	Fairly narrow and intense
5922	Hazy and faint
5946	Narrow, intense
5968	Wide, faint, and hazy
6265	Wide, moderately intense
6290	Narrow, faint
6325	"
6375	"
6775	Wide, faint
6796	Narrow, faint
6815	"
6838	Moderately intense
6860–6900	Band, shading towards red
6922	Moderately intense
7422	Narrow, intense band

It is, of course, evident that the spectrum of the solutions of neodymium chloride dissolved in methyl or ethyl alcohol

is very different from that of the andydrous salt. It seems reasonable to suppose that if the molecules of the salt in the nonaqueous solutions exist in the free state, that is, not combined with the solvent in any way, they should give about the same spectrum as they do when in the state of the dry powder. Since they do not do this, we must suppose that the solvent plays an important rôle in determining the character of the absorption, and how it can do this without being combined with the salt in some way is not easy to understand.

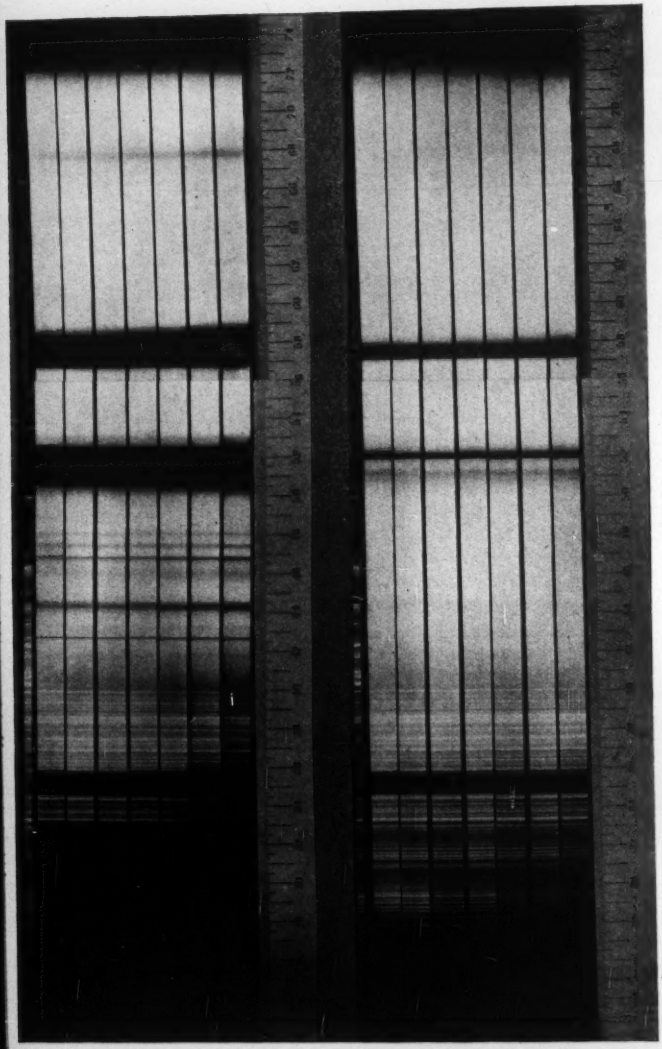
Neodymium Bromide in Water—Beer's Law (*See Plate XVIII.*).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.3, 1.7, 1.15, 0.77, 0.54, 0.38, and 0.29; the corresponding depths of absorbing layer were 3, 4, 6, 9, 13, 18, and 24 mm. For B the concentrations were 0.57, 0.42, 0.29, 0.19, 0.13 0.09, and 0.07; the depths of the absorbing layer were the same as in A.

The bromide solutions are very much redder in color than those of the chloride or nitrate. Judging from the color alone, one would say that the nitrate solutions are much more transparent in the blue and violet than the chloride, and the chloride solutions much more so than those of the bromide. The spectrograms do not show this, at least not very clearly, which merely indicates that where full exposures are given, slight general absorption is not recorded by the photographic plate. A spectrophotometric comparison of the light transmitted through these solutions, such as is now in progress in the present work, will undoubtedly show this general absorption of the bromide solutions in the more refrangible portion of the spectrum.

In studying the spectrograms of this plate, A was compared with Plate XI., B, and B with Plate XII., B; that is, the spectrum of the bromide solutions was compared with that of a chloride solution whose concentration, in each case, was almost exactly 1.5 times that of the bromide solution, the depth of the absorbing layer being the same in both cases. The two spectra are found to be almost identical, except in

Plate XVIII.



A B

the extreme ultraviolet, where the bromide solutions absorb much more strongly. The limits of transmission for the most concentrated and most dilute solutions of A are λ 3270 and λ 3050, respectively, whereas the corresponding chloride solutions transmitted to beyond λ 2500. The ultraviolet absorption shown by B is about the same as that of the chloride solutions used in making Plate XI., B.

The absorption bands have in general about the same intensity and character in the bromide solutions as they have in the corresponding solutions of the chloride, indicating a considerably greater absorbing power of the bromide, since the concentrations of its solutions were only 0.66 of that of the chloride. A small part of this is due to the fact that the negatives of Plate XV. were not as fully developed as those made with the chloride solutions, but even if the development had been exactly the same, the bands of the bromide solutions would only have been very slightly less intense than those of the chloride solutions, so we must conclude that in solutions of the same concentration the bands of the chloride solution would have only about 75 per cent of the intensity of the same bands in the spectrum of the solution of the bromide.

It will be remembered that the very concentrated solutions of the chloride showed some slight deviations from Beer's law, the absorption to the red side of the narrow band at λ 4275 being described in some detail. The deviations from Beer's law are smaller in the bromide solutions, perhaps because the concentrations are less. No shading or fine absorption line between λ 4275 and λ 4290 is to be seen in the spectra of even the most concentrated solutions used in making the negative for A of Plate XVIII. The shading on the red side of the yellow band narrows somewhat with increasing dilution, but not quite as rapidly as was the case with the chloride.

Neodymium bromide was dehydrated in a current of hydrobromic acid and dissolved in methyl alcohol, and also in mixtures of methyl alcohol and water. The solution in methyl alcohol was stable, and showed the same spectrum as a solution of the chloride in the same solvent. On adding water,

precipitates were formed, indicating some chemical change. These were filtered out and a spectrogram made to see whether the same changes that we observed with the chloride take place in this case. This spectrogram is not reproduced, but it indicated that the changes which were produced were, quantitatively as well as qualitatively, the same as those we discussed under Plates XV. and XVI.

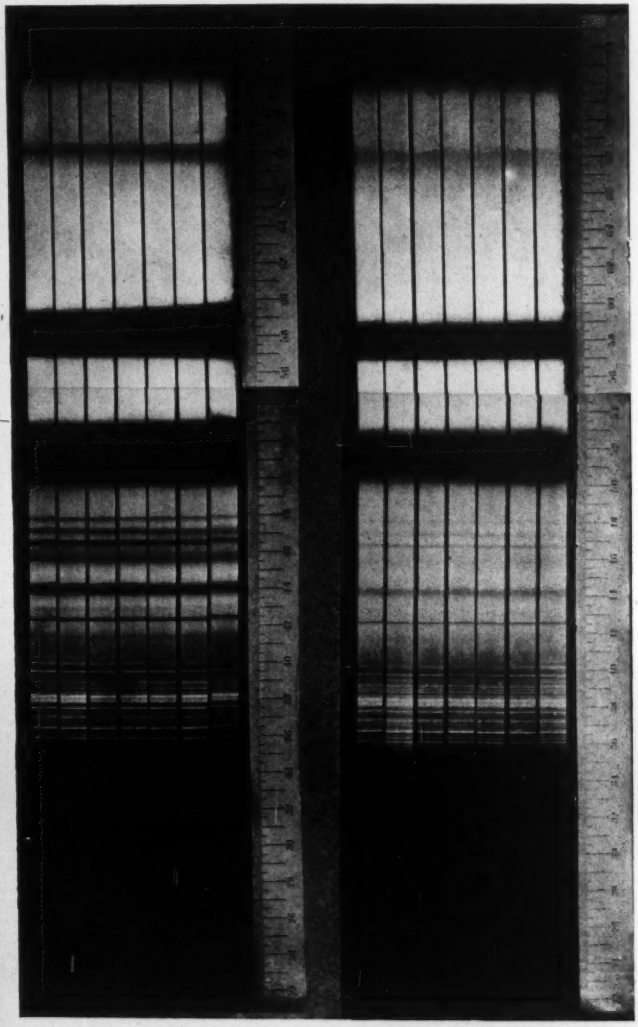
Neodymium Nitrate in Water—Beer's Law (See Plates XIX. and XX.).

The concentrations of the solutions used in making the negative for A, Plate XIX., beginning with the one whose spectrum is adjacent to the numbered scale, were 2.96, 2.22, 1.48, 0.99, 0.69, 0.50, and 0.38. For B the concentrations were 1.48, 1.11, 0.74, 0.50, 0.35, 0.25, and 0.19. For A, Plate XX., they were 0.74, 0.55, 0.37, 0.25, 0.175, 0.125, and 0.095; and for B, 0.37, 0.275, 0.185, 0.125, 0.092, 0.062, and 0.048. The depths of absorbing layer were in each case 3, 4, 6, 9, 13, 18, and 24 mm.

The nitrate solutions are much less yellow than the chloride solutions, having, when concentrated, a decided pinkish tint, indicating greater transparency in the violet region of the spectrum.

The spectrum of the nitrate solutions, especially when the concentration is considerable, differs quite a little from that of the chloride. It is true that at first glance they seem identical, for wherever there is a band in the spectrum of the chloride solution a band is found in the nitrate solution; but, at least in concentrated solutions, the bands have a very different appearance. The general difference is that the nitrate bands are much broader and hazier than those observed with the chloride. With dilution the spectrum of the nitrate changes very much more than that of the chloride, which we found was practically unchanged when the concentrations were varied from about 1.5 normal to near zero. The spectrum of the nitrate solutions changes somewhat, even in B, Plate XX., where the concentration ranges from 0.37 to 0.048 normal.

Plate XIX.



A B

Instead of giving a detailed description of the spectrum of the nitrate, we will limit ourselves to a description of the changes which take place in a few of the bands differing most from the corresponding bands in the spectrum of the chloride solution.

Let us consider first the band at λ 4275. In the spectrum of the chloride solution this band has a width of only a few Angström units, and is very intense. In the most concentrated nitrate solution this band has a width of 15 A.U. and its center falls at about λ 4280. Its edges are rather hazy, but the band is very nearly symmetrical. With increasing dilution the violet edge increases in intensity, taking more and more the form of a narrow absorption line with center at λ 4275, while the red portion of the band decreases in intensity, and at a concentration of 0.38 and a depth of layer of 24 mm. it has taken the form of a slightly hazy band with its center near λ 4282. This band is here clearly separated from the more intense and narrow one at λ 4275. With a concentration of 0.19 normal and a layer 24 mm. deep, the λ 4282 band has become a mere shade on the red side of the λ 4275 band, and finally, with a concentration of 0.048 and a 24 mm. layer of the solution, it is no longer visible on the photograph.

At λ 4330 or λ 4335 the concentrated chloride solutions show a rather wide hazy band, the intensity of which is not sufficient to allow it to be seen in solutions of less than 1.0 normal with a depth of layer of 5 mm. or less. The more dilute solutions of the nitrate used in making A, Plate XIX., show this band with about the same intensity and character that it has in solutions of the chloride, while the very concentrated nitrate solutions show it very faintly; that is, the band increases in intensity with dilution. In fact, it behaves very much like the λ 4275 band, indicating that the two owe their origin to the same "absorber."

The 3.4 normal chloride solution in a layer 3 mm. deep shows a band at λ 4760, to which the following description applies: Absorption begins at λ 4750, rises gradually to a maximum at λ 4760, then gradually falls to zero at λ 4770. This band remains practically constant throughout the series

of solutions used in making B, Plate XI., showing that it is practically unaffected by change in concentration.

The 2.96 normal solution of the nitrate, with a layer 3 mm. deep, shows, in the same region, a band which has the following characteristics: Absorption begins at λ 4730, rises to a maximum at λ 4737, then falls to a slight minimum at λ 4742, from which it again rises to a maximum at λ 4755, falling off gradually to zero at λ 4780, with indications of a faint minimum near λ 4765. We really have then to deal with a group of three bands, their centers being approximately at λ 4737, λ 4755, and λ 4772. With dilution the bands at λ 4737 and λ 4772 rapidly lose their identity, while the band whose center was at λ 4755 increases in intensity and somewhat asymmetrically; so that in the solution whose concentration was 0.99, with a depth of layer of 9 mm., there remained but a single band, having its center at λ 4760, and shading off towards both sides a little more than the corresponding band in the chloride solution. With increasing dilution this band also becomes more and more like the λ 4760 chloride band.

The chloride solution whose concentration was 1.7 normal, with a layer 3 mm. deep, showed a deep, narrow absorption band at λ 5090, and a wide, somewhat hazy one with its center at λ 5125. There was a region of transmission between the two about 15 A.U. wide. A, Plate XVI., shows that these bands do not change materially with dilution to 0.22 normal. The corresponding nitrate solution also shows a band at λ 5090, but it is much wider and hazier than in the chloride solution, while the λ 5125 band is, if anything, narrower. The two bands are not clearly separated in the first strip of B, Plate XIX. With dilution, however, the λ 5090 band narrows down and becomes a little fainter, while the λ 5125 band widens a little towards the red, so that in rather dilute solutions the bands present the same appearance as they do in the corresponding chloride solutions. The region λ 5200 to λ 5240 shows practically continuous absorption with very hazy edges in the first strip of B, Plate XIX.; with dilution this changes rapidly, indicating bands somewhat similar to those of the chloride solutions belonging to A, Plate XII.

Plate XX.

A B

In A, Plate XX., the band has broken up, and instead of showing two narrow intense bands at λ 5205 and λ 5222 it shows the following: There is a deep, narrow band at λ 5205, a wider and very much more intense one at λ 5225, and a rather narrow, intense band at λ 5235. With increasing dilution the λ 5235 band diminishes in intensity, practically disappearing in the most dilute solution used in making B, Plate XX. At the same time λ 5225 decreases somewhat in intensity and rather more on the red than on the violet side, so that when the most dilute solution of B, Plate XX., is reached its intensity is only slightly greater than that of the λ 5205 band and its center is at about λ 5222. Here also, then, we find the same general tendency for the spectrum of the nitrate solutions to change with dilution so as to become more and more like that of the chloride and bromide solutions.

We might go on and give in detail the changes taking place in the bands located in the yellow, orange, and red, since the changes here are just as well marked as those we have already described. But they all point to the same thing, namely, the dissimilarity of the spectra of concentrated solutions, and the gradual change of the nitrate spectrum into that of the chloride or bromide with decreasing concentration. That the spectra of dilute solutions should become more and more alike with increasing dilution was, of course, to be expected from the theory of dissociation; but on the simple theory of dissociation no one could have predicted that the chloride and bromide should give spectra which are practically identical, both in concentrated and in dilute solutions, while the nitrate should behave so differently, especially as it is well known that the three dry salts have quite different absorption spectra.

Our work on the spectrum of neodymium chloride in mixtures of alcohol and water made it seem very probable that the molecules as well as ions of the salt in solution are solvated, that is, have combined with them a relatively large number of molecules of the solvent. On this view, the results with aqueous solutions of the chloride, bromide, and nitrate are just about what we ought to expect, if we assume that the absorption bands are due to electrons which are located

in, or closely associated with the neodymium atom. Let us consider this a little more fully, even at the risk of repeating certain things we have said before.

Let the neodymium atom contain electrons which, if the atom is by itself, would respond to light waves of certain definite frequencies. White light, after having been acted on by a number of such atoms, would, when analyzed by a prism or grating, show a certain number of absorption bands whose wave lengths could be determined. If, now, the atoms, instead of being free, are each united to 3 chlorine atoms, these foreign atoms would affect the periods of the neodymium electrons and we should expect to find the absorption spectrum modified. If the neodymium atom were combined with 3 bromine atoms instead of chlorine, we should expect a somewhat different spectrum again, and so on for the various salts; each one would be characterized by its own absorption spectrum. If these salts could be dissolved in some medium which had no action on them other than to allow their molecules to move about freely, we should not expect any material change in the spectrum, while if the solvent united with them, forming solvates, we should expect the spectrum to be modified.

In a solvent like water, where it is probable that rather complex hydrates are formed, the effect of the solvent might even become *the* most important factor in determining the character of the absorption. To take a concrete case, suppose each molecule of a salt of neodymium in aqueous solution is united with 10 molecules of water. If the salt is the chloride or bromide, each neodymium atom has only 3 foreign atoms to disturb the periods of its electrons besides the 30 atoms in the combined water; while if the salt is the nitrate, it would have 12 foreign atoms besides those of the water. Evidently these 12 atoms would have a very much greater effect than the 3 in the case of the chloride or bromide, if we assume that the general arrangement in space is not very different in the two cases. We see, then, that the fact that the spectrum of the nitrate in aqueous solutions of considerable concentration is different from that of the chloride or bromide is what we should expect, and we also see that the

very slight change in the spectrum of the bromide and chloride on dilution, as compared with the great change in case of the nitrate, might almost have been predicted.

The change taking place with dilution is, of course, due to dissociation, each neodymium atom, after dissociation, being simply united with, say, 10 molecules of water, the anion of the molecule having left it. The neodymium ions in dilute solutions are therefore the same, no matter what salt is in solution, if we assume that the presence of the anions in the solution does not influence the hydrating power of the metallic ion. Other things being equal, therefore, we should expect that aqueous solutions of those salts whose molecules are made up of only a very few atoms united with a neodymium atom should show the least change in the spectrum when the concentration is varied, since the removal of the few atoms making up the acid radical from the hydrated molecule would in general have but a slight effect on the periods of the absorbing electrons in the metallic atom. Water solutions of salts whose molecules consist of a great many atoms united with a neodymium atom, like the nitrate, acetate, or sulphate, ought to show a considerable change in their spectra as a result of dissociation, since the removal of the great number of atoms forming the acid radical would undoubtedly have a marked influence on the periods of the absorbing electrons.

It is plain, therefore, that the simple theory outlined above furnishes a perfectly simple and rational explanation of all the phenomena which have thus far been observed in the study of the absorption spectra of neodymium salts. That it also suffices for salts of the other rare earths studied will appear in what follows.

Neodymium Nitrate in Methyl Alcohol—Beer's Law (*See Plate XXI.*).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.80, 0.64, 0.50, 0.40, 0.32, 0.25, and 0.20, and for B they were 0.32, 0.25, 0.20, 0.16, 0.13, 0.10, and 0.08; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm. in both cases.

On account of the NO_3 band the spectrum terminates at λ 3250 in the ultraviolet for A, and at about λ 3200 for B.

The absorption near λ 3500 resembles that shown by aqueous solutions much more nearly than was the case with the chloride. Only two bands appear, their positions being λ 3465 and λ 3545, respectively. The general shading extends from about λ 3450 to λ 3570.

The bands in the blue and violet are not as intense as the corresponding bands in the alcoholic solution of the chloride. In position and general character they are much more like those shown by concentrated solutions of the nitrate in water. There is a band at λ 4280, about 10 A.U. wide and not specially intense. At λ 4430 is a wide, faint band, and there is a similar one at λ 4600. Three faint bands show at λ 4690, λ 4735, and λ 4825, resembling very much the three corresponding bands in concentrated aqueous solution. The intensity here is, however, much less.

In the aqueous solution we found bands at λ 5205, λ 5225, and λ 5235. The first one was evidently due to the cation, the second, partly to the cation and partly to the molecule, while the one at λ 5235 was apparently due only to the nitrate molecule. In the methyl alcohol solution, we find only a weak shade in the region λ 5200, while at λ 5225 and λ 5240 there are two rather narrow, intense bands. There is considerable shading to both sides of these bands.

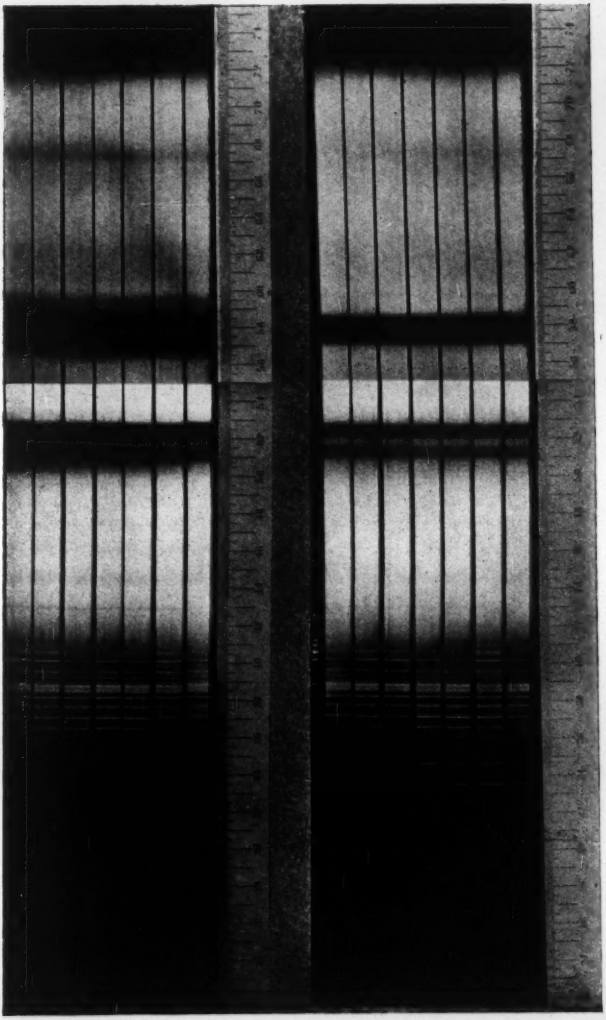
In the yellow, A shows absorption from λ 5700 to λ 5870, shading off towards the red, with a band at λ 5965. B shows a band at λ 5720, which is perhaps double; deep absorption from λ 5755 to λ 5845, with faint bands at λ 5760 and λ 5835; and a very intense band at λ 5790.

The spectrum ends near λ 7320 in a band which does not seem especially intense.

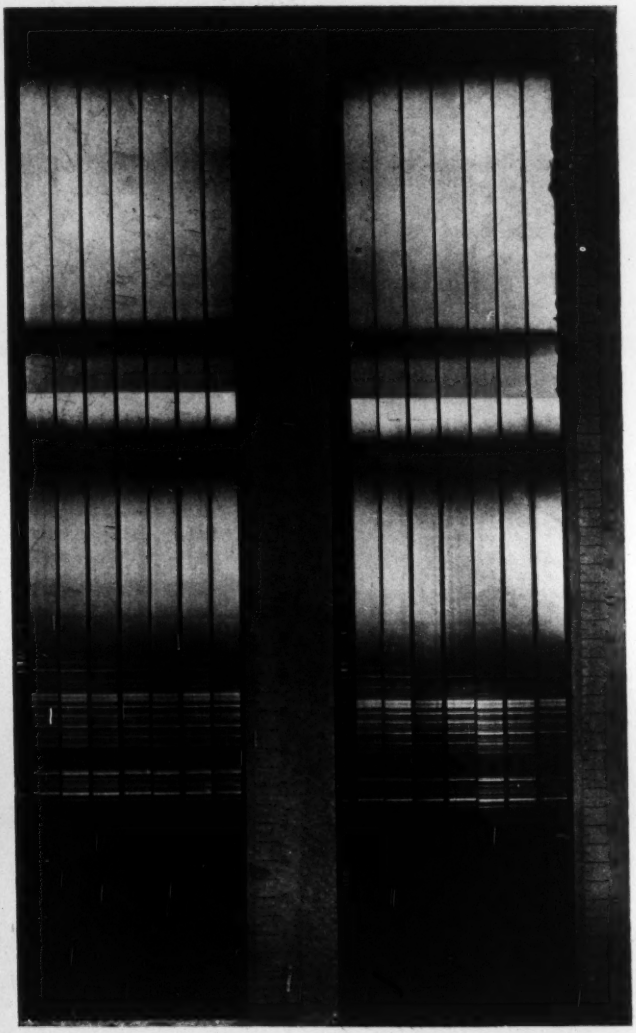
Neodymium Nitrate in Ethyl Alcohol—Beer's Law (*See Plate XXII.*).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 0.32, 0.26, 0.20, 0.16,

Plate XXI.



A B



A B

0.13, 0.10, and 0.08, and for B they were, in the same order, 0.16, 0.13, 0.10, 0.08, 0.06, 0.05, and 0.04; the corresponding depths of absorbing layer were 6, 7.5, 9.5, 12, 15, 19, and 24 mm.

The solutions used in making A of this plate were of the same concentrations as those used in making B of Plate XXI., and as the depths of absorbing layer were also the same, the two plates are directly comparable.

The two spectra are very similar, but nevertheless there are some well-marked differences. The bands at λ 5225 and λ 5240, which were quite sharp and intense in the methyl alcohol solution, here show simply as one hazy band of moderate intensity, its middle being near λ 5235. Even in B, where the concentration is much less, this band does not break up into two, but simply diminishes in intensity without change of character.

The yellow group shows a wide, faint band at λ 5730 and a moderately intense band at about λ 5790, much less intense and sharp than in methyl alcohol. There is a pair of poorly-defined bands at λ 5825 and λ 5845, apparently corresponding to the band at λ 5835, observed in the solutions in methyl alcohol.

The spectrum ends at λ 7315 in a band which is not very intense or sharp. In general, the absorption in the two alcohols is about the same, the general tendency being for all absorption bands to be narrower in the methyl than in the ethyl alcohol solutions.

Praseodymium Chloride in Water—Beer's Law (*See Plate XXIII.*).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 2.56, 1.92, 1.28, 0.85, 0.60, 0.42, and 0.32. For B the concentrations were 0.85, 0.63, 0.42, 0.28, 0.20, 0.14, and 0.11, the depths of absorbing layer being 3, 4, 6, 9, 13, 18, and 24 mm. respectively.

The solutions of praseodymium chloride are all green or yellowish-green, only the intensity of the color changing with change in the concentration.

For these solutions Beer's law holds very closely, excepting for the extreme ultraviolet absorption in A, and the yellow bands in the two or three most concentrated solutions of A.

The limits of transmission in the ultraviolet, for the most concentrated and most dilute solutions of A, are λ 2720 and λ 2650, respectively. The edge is fairly sharp, indicating the presence of a rather intense band. This is also indicated by B, where the spectrum ends abruptly at λ 2630, the limit being the same for all of the solutions.

The absorption bands shown in A are as follows: λ 4380 to 4480, strong band with red edge somewhat shaded; λ 4640 to λ 4710, sharp on red side, quite diffuse towards the violet; λ 4800 to λ 4830, sharply defined on both sides; λ 5860 to λ 5950, both edges diffuse; λ 5985, fairly narrow band with diffuse edges. The region between this band and the principal yellow one shows very strong absorption.

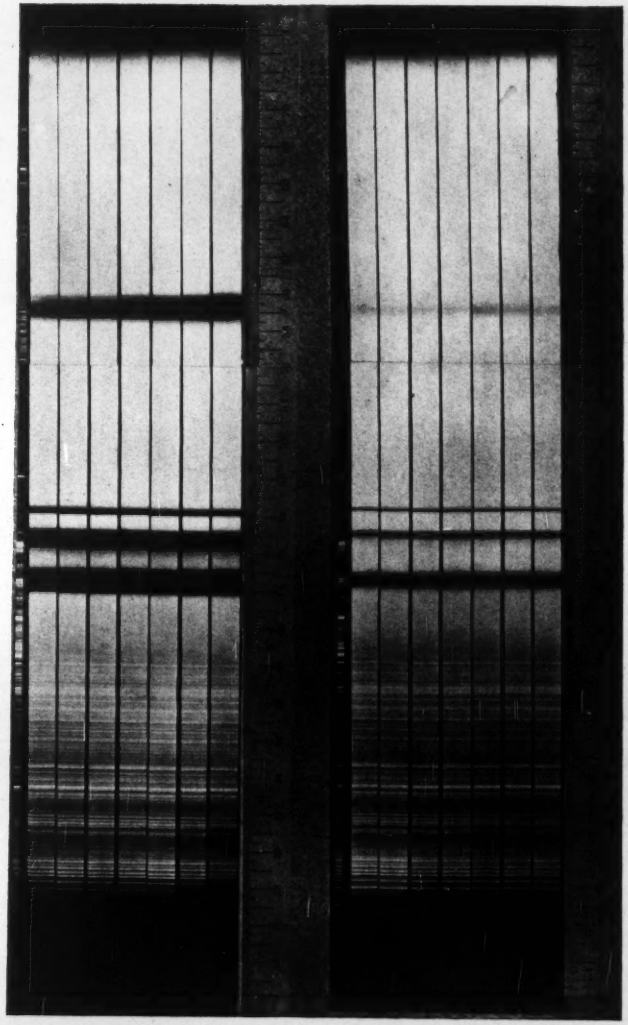
B shows the following: λ 4410 to λ 4465, both edges a little diffuse; λ 4685, fairly narrow band, still more diffuse towards the violet, although somewhat shaded also towards the red; λ 4815, narrow band, with edges slightly shaded; λ 5900, wide hazy band, absorption not complete, even at its middle; λ 5985, rather faint, hazy band.

The greenish tinge of the solutions would suggest that there is considerable general absorption in the red, because the absorption in the yellow is not sufficient to impart any marked color to the solution, and the bands in the violet and blue could only give it a yellow tint. The negative for A does, in fact, show pretty strong general absorption from λ 7100 to the end of the red, but no doubt a spectrophotometric study of the solutions would show general absorption much farther down into the red. The negative for B shows no sign of this absorption, for very obvious reasons.

Praseodymium Chloride in Mixtures of the Alcohols and Water (*See Plate XXIV.*).

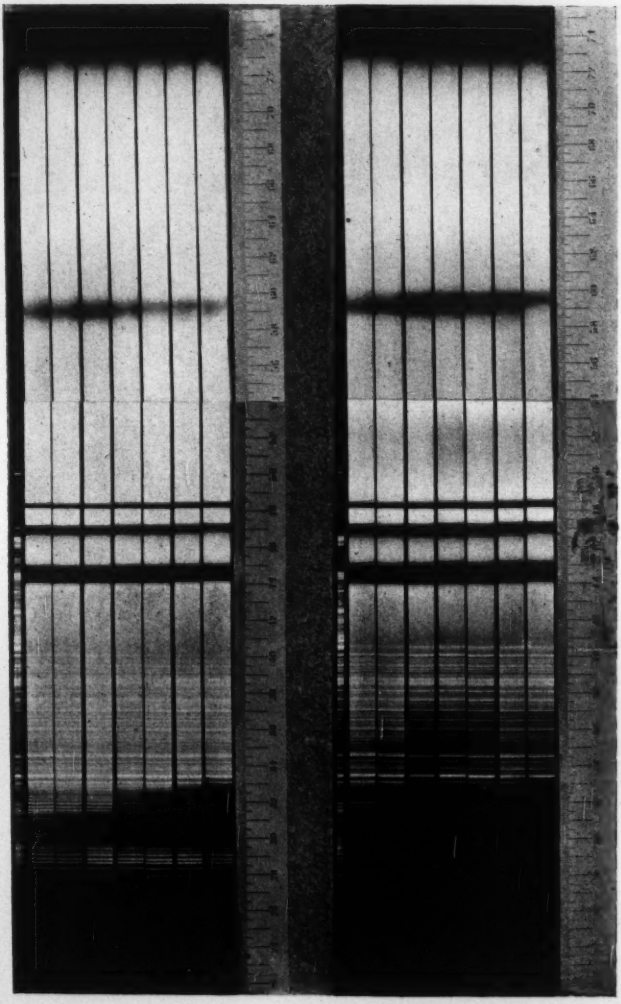
The concentration of the praseodymium chloride was constant throughout and equal to 0.5 normal. The percentages of water in the solutions, beginning with the one whose spec-

Plate XXIII.



A B

Plate XXIV.



A B

trum is adjacent to the numbered scale, were 0, 2.3, 5.6, 8, 10.6, 13.3, and 16. The depth of absorbing layer was 1.0 cm. Methyl alcohol was the chief solvent in the solutions pertaining to A, while ethyl alcohol was employed in the solutions used in making the negative for B. The two spectrograms are identical, except for a little greater general absorption in the ultraviolet with the ethyl alcohol. The most striking feature of the spectrograms is the appearance of the intense absorption band near λ 3000 as the percentage of water is gradually decreased. Only a faint trace of this band is visible with 16 per cent of water in the solution, and the band is comparatively weak even with only 8 per cent of water. From this point it increases very rapidly in width and intensity with decrease in the amount of water, until in the pure alcohol solutions its limits (transmission) are λ 2970 and λ 3230, this being by far the most intense band in the whole spectrum.

The bands in the violet and blue apparently shift somewhat towards the red, this being, due, however, to the fact that the alcohol bands are a little nearer the red end of the spectrum, and that when the percentage of water changes from 16 to 0, the two sets of bands coexist, but are far from being separated. The change is exactly the same in character as the one described in detail in discussing the λ 4760 band for neodymium chloride in mixtures of alcohol and water.

The positions of the bands in the solution containing 16 per cent of water are as follows: λ 4390 to λ 4470, λ 4660 to λ 4700, λ 4800 to λ 4825. In the solution in pure alcohol they are λ 4410 to λ 4480, λ 4690 to λ 4715, λ 4810 to 4840. Hence, it appears that the two most refrangible bands have a slightly greater width in the water solution, while the λ 4815 band is more intense in the alcoholic solutions.

The bands in the yellow show very well, indeed, the fact that here, as in the spectrum of neodymium chloride, we have the coexistence of two sets of bands when the water content of a 0.5 normal solution is in the neighborhood of 8 per cent. The band in the yellow has already been described under Beer's law, but as the concentration and depth of layer are

different here, the following will serve to indicate what the spectrum of the 16 per cent water solution shows. Absorption begins at λ 5850 and rises to a maximum at about λ 5900, then decreases to a minimum at λ 5950, from which it again rises to a maximum at about λ 5980, falling off to zero at λ 6000. The solution in pure alcohol shows the following: Weak absorption begins at λ 5800 and continues without material change up to λ 5880, where it falls almost to nothing. At λ 5900 it begins to increase and reaches a strong maximum at λ 5955, falling off gradually to zero at λ 6000. The intermediate solutions show the gradual disappearance of the bands characteristic of the aqueous solution, and the increase in intensity of those belonging to the alcoholic solution, as the percentage of water is gradually decreased. The maximum change takes place from the fifth to the third strips, counting from the numbered scale, indicating here, as with neodymium chloride, that the two sets have about half their normal intensity when the water content of the solution is about 8 per cent, or when the solution contains about 10 molecules of water per molecule of the dissolved substance.

Praseodymium Nitrate in Water—Beer's Law (*See Plate XXV.*).

The concentrations of the solutions used in making the negative for A, beginning with the one whose spectrum is adjacent to the numbered scale, were 3.2, 2.4, 1.6, 1.1, 0.75, 0.53, and 0.41. For B the concentrations were 1.1, 0.80, 0.55, 0.33, 0.26, 0.18, and 0.14; the depths of absorbing layer in both cases were 3, 4, 6, 9, 13, 18, and 24 mm.

There is a great deal of absorption in the ultraviolet, the spectrum of the most concentrated solution ending at λ 4000, while that of the four most dilute solutions of set A ends at about λ 3650. The spectra shown in B all end at λ 3570. This absorption is not to be ascribed to the NO_3 radical, as its band lies beyond λ 3300 in all the solutions thus far studied.

The absorption bands do not differ materially from those of the chloride, except that they are a trifle more intense, owing, no doubt, to the slightly greater concentration of the nitrate solutions. Also, the violet and blue bands show a

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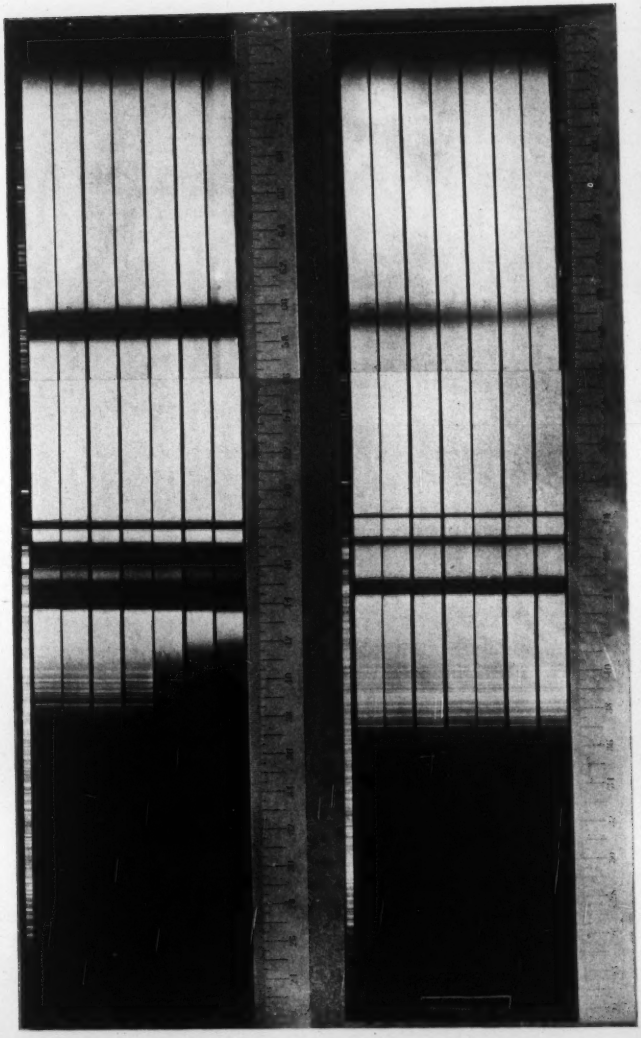
Plate XXV.



A B

slight deviation from Beer's law in the two or three most concentrated solutions of A.

It may be said in general that the absorption spectra of the different salts of the same metal resemble each other very closely; and it is only when careful attention is paid to the structure of each individual band, or group of bands, that the differences are brought out clearly. In the process of printing and reproducing the spectrograms illustrating this section, a great deal of the finer detail has been lost, and as it is just this detail which shows the differences alluded to above, it is clear that in many cases the reproductions fail entirely to show the important points. In cases of special importance a rather full description of the appearance of the negatives has been given in the text. A full description of this nature covering all the spectrograms of the present chapter would require an amount of time and space which would be quite prohibitive and unwise.

It is hoped, however, that the plates, together with the description given in the text, will make clear the points which we have tried to emphasize most strongly, *viz.*:

1. That the absorption spectra of different salts of the same metal in the same solvent are different if the concentration is great, or, more generally, if the dissociation is only slight; and that as the dissociation becomes more and more complete, they become more and more alike.

2. That the absorption spectra of the same salt in different solvents are in general different.

3. That with change in dissociation of the salt in any one solvent, the change in the absorption spectrum of salts having anions containing only a few atoms, such as the chloride and bromide, is very slight; but that as the complexity of the anion increases, the change becomes more and more pronounced.

4. That when a salt is dissolved in mixtures of two solvents, the relative percentages of which are varied, there is not a gradual change of one spectrum into the other; but the spectrum given by the mixture is a superposition of the two spectra, the two sets of bands existing together. If the salt is one whose spectrum changes considerably with its state of dis-

sociation, we have in addition to the above phenomena the changes due to the varying dissociation of the dissolved salt produced by the varying composition of the mixture.

The explanation of these points on the working hypothesis which has guided the present work has already been given in the discussion of Plates XIX. and XX.

In the introduction to the present section the work of Helen Schaefer was referred to. It will be recalled that she studied the spectrum of the nitrate of neodymium in various solvents, and also in mixtures of two solvents, the case to which she calls special attention being mixtures in various proportions of water and acetone. She did not come to the conclusion which we have reached, that in such mixtures we have two distinct sets of absorption bands, since she considers that the bands shift gradually, some in the direction demanded by Kundt's law, and some in the opposite direction. There are two reasons why she did not draw the same conclusion that we have reached. In the first place she worked with the nitrate, which we have found shows a considerable variation in its spectrum with change in dissociation, and her solvents being water and acetone, the change in the dissociation would be very considerable. For this reason, she found a continuous change in the spectrum as more and more acetone was added, which was just what she expected. Had she worked with the chloride or bromide she would have found practically no change until the proportion of the nonaqueous solvent in the mixture had become very great, and in this event her conclusions would have been quite different.

In the second place her salts were not dehydrated (if they were, she makes no mention of the fact), and hence even in the solution in pure acetone she probably had from 6 to 10 molecules of water per molecule of the dissolved salt, which we have found will give the spectrum characteristic of the nonaqueous solvent with only about half its normal intensity. It is not very surprising, therefore, that she failed to discover the coexistence of the two sets of bands, which would have given a perfectly simple explanation of all the phenomena that she observed.

SUMMARY AND CONCLUSIONS.

It is evident from the spectra of the solutions studied in the present investigation that deviation from Beer's law is the rule rather than the exception. Of the great number of sets of solutions studied, only a very limited number appear to conform to Beer's law, and it is possible that with more exact spectrophotometric measurements this number would be reduced still further. This is exactly what we should expect, since actual solutions always contain more than one kind of "absorber," and the relative concentrations of these "absorbers" are continually changing with change in concentration of the solution. Beer's law could hold, as explained in the introductory section, only in cases where the relative concentrations of the different kinds of absorbers do not change with dilution, or where the absorption of all the different kinds of absorbers is identical. The first one of these conditions is perhaps never fulfilled, while the second one is undoubtedly approached more or less closely in certain cases, such as in aqueous solutions of neodymium chloride or bromide or of praseodymium chloride. The rule is, however, that the different absorbers have different absorbing powers, and the problem is, therefore, to decide which absorbers are responsible for the bands observed in the various spectra.

According to the theory of Ostwald, which is simply Arrhenius's dissociation theory applied to the absorption spectra of solutions, we have but two or three kinds of absorbers, namely, the molecules of the dissolved salt and one or both of the ions formed from it. In the case of all the salts studied in the present work, excepting the nitrates, the anion was colorless; so all the absorption, according to Ostwald's theory, should be due to two kinds of absorbers, the molecule and the cation. That this theory fails to account for the deviation from Beer's law observed in the ultraviolet absorption of copper salts, the red bands of cobalt salts, the ultraviolet band of cobalt chloride, and the absorption of iron chloride, has already been pointed out, for all these bands narrow with dilution, even when the number of molecules in the path of the beam of light is kept constant. Whether

this theory is able to account for the behavior of those bands which narrow with dilution when the conditions for Beer's law obtain, but which widen when molecules are kept constant, can only be decided by spectrophotometric measurements.

The work of Müller on salts of nickel and copper shows that the behavior of the red absorption band of these substances can not be accounted for on Ostwald's theory, and this makes it at least very probable that the same will be found for salts of other metals. Ostwald's theory may, therefore, be dismissed, not because it is erroneous, but because it is incomplete. It leaves out of account certain changes taking place in solutions, which produce other "absorbers" than those which it considers.

The other theories which aim to account for the deviations are of two kinds, *viz.*:

(1) Those that assume that the increased absorption in concentrated solutions is due to the formation of aggregates of the molecules of the dissolved substance, or of the molecules and the ions into which they break down on dissociation.

(2) Those that assume that the deviation is due to the formation of solvates, that is, combinations of the parts of the dissolved substance with the molecules of the solvent.

It has been shown by Hartley and other workers who have studied the change in the absorption with the change in temperature that the bands which widen with increase in concentration (conditions for Beer's law assumed to obtain) also widen with rise in temperature; that is, rise in temperature produces very much the same effect as increase in concentration. This seems to us pretty conclusive evidence against the theories which are based on the formation of aggregates, for it is well known that the change in the aggregates produced by rise in temperature is *not the same* as that produced by increase in concentration, but *exactly the opposite*.

The theories which assume the formation of solvates are not open to this objection, because it is well known that the change in the solvates produced by rise in temperature is in general the *same* as that produced by increase in concentration. As a solution becomes more concentrated the solvates

become simpler and simpler, that is, fewer molecules of the solvent are combined with each part of the dissolved substance. Rise in temperature also breaks down complex solvates into simpler ones. Of course, it does not follow that the solvates in a solution of concentration c, at temperature t, are *exactly* the same as those in a solution of concentration c_2 at a temperature t_2, since under the changed conditions it may happen that the particular solvates which were most stable when the conditions were c and t, may be less stable than solvates of nearly the same composition at c_2, t_2.

For this reason, and also because *our work on neodymium and praseodymium salts in mixed solvents seems almost conclusive evidence in favor of the existence of solvates*, we have used the solvate theory as a working hypothesis throughout this work. That it is not far from being correct is shown by the fact that all the phenomena observed in the great number of solutions studied are accounted for without anything but the simplest assumptions in regard to the behavior of the solvates in question.

We shall now summarize briefly the main points brought out in the present work.

Solutions of cobalt salts have, in general, three regions of absorption in that part of the spectrum which can be photographed without resorting to other means than the commercial dry plate. One is in the extreme ultraviolet, and we concluded that it is due to the molecules of the dissolved substance. Their absorption is influenced to some slight extent by solvation, but differently for the different salts. That no part of this absorption is due to the cobalt ions is shown by the fact that solutions of cobalt sulphate are perfectly transparent beyond λ 2200, although they are dissociated to a very considerable extent.

Another region of absorption is in the green, near λ 5200, for most solutions. This band, which is the most characteristic one of the cobalt solutions, was ascribed by Ostwald to the cobalt ion. That the molecules also absorb in this region, and in fact have a greater absorbing power than the ion, has been abundantly shown. Whether the simple theory

of dissociation is able to account for the observed deviations from Beer's law for this band is not known, but it is improbable. The question is now being investigated in this laboratory and a definite answer will probably be given in the near future.

The absorption band at λ 3300 in the spectrum of the aqueous solution of cobalt chloride, since it disappears with dilution even when molecules are kept constant, cannot be due to the cobalt chloride molecules, but we found good reasons for thinking that it is due to some hydrate of these molecules which is formed in solutions of moderate concentration even at ordinary temperature. The two bands in the same region which appear in the alcoholic solutions of the same salt behave so much like the band in the aqueous solution that they are undoubtedly due to some relatively simple alcoholate.

The bands in the red region of the spectrum of solutions of cobalt salts we concluded were due to very simple solvates, such as are formed only in the most concentrated aqueous solutions, or in solutions of moderate concentration but at very high temperatures. Donnan and Bassett assumed that these bands are due to some complex anions, such as $CoCl_2.Cl$ or $CoCl_2.Cl_2$, which would then be the same in aqueous and nonaqueous solutions. There are a great many objections to this explanation. In the first place, such complexes ought to obey the usual rule for aggregates, that is, they ought to break down with rise in temperature, whereas the change in the spectrum demands the opposite. In the second place, according to this theory the bands ought probably to be the same in aqueous as in nonaqueous solutions, which we have found is not the case. *On the theory of solvates, however, everything is perfectly clear.* The differences in the structure of the group of bands with different solvents is what we should expect, and the appearance of the bands with rise in temperature of aqueous solutions, or with the addition of large quantities of a dehydrating agent, is simply due to the formation of the required simple hydrates under these conditions.

The bands of solutions of nickel salts are all of the same type as the green cobalt band, and, hence, must be studied

spectrophotometrically. The change in the ultraviolet band with addition of dehydrating agents, however, suggests that here also hydrates play an important part. Anhydrous nickel chloride could not be dissolved in the nonaqueous solvents used, hence the work was of necessity limited to aqueous solutions.

With the exception of copper chloride in acetone, which has a band at λ 4700, all copper solutions show only two regions of absorption, one in the ultraviolet and one in the red. The ultraviolet band, since it narrows rapidly with dilution even when molecules are kept constant, cannot be accounted for on the simple theory of dissociation. And as it widens rapidly with rise in temperature, we must conclude that it is due to the solvated molecules, the absorbing power of which increases rapidly with decrease in the complexity of the solvate.

The band in the red belongs in the same class with the green cobalt band. But, as mentioned above, Müller came to the conclusion that dissociation is unable to account for its deviation from Beer's law. This also agrees with what we found in studying its behavior in mixtures of alcohol and water in the case of the chloride. Hence, we assume that solvates here also play a rôle, which, however, is not quite so apparent, owing to the fact that both the solvated ions and the molecules absorb light in this region.

Another fact which supports our view is that the absorption in the red is not widely different in different solvents, provided the concentrations are about the same; while in the ultraviolet the absorption is many times greater in the nonaqueous than in the aqueous solvents, the reason for the latter being, first, that the dissociation is much greater in aqueous than in nonaqueous solutions, and hence, for equal concentrations, the number of molecules in the latter is much greater than in the former. Secondly, the solvating power of water is much greater than that of the nonaqueous solvents used, and hence the comparatively few molecules present, by forming relatively complex hydrates, suffer a still further reduction of the absorbing power.

The only salt of iron studied was ferric chloride. It shows

only one region of absorption, namely, the one which cuts off the entire ultraviolet, and usually also the violet and blue portion of the spectrum. In aqueous solutions this absorption band narrows very rapidly with dilution, even when molecules are kept constant, indicating a marked effect of hydration. In alcoholic solutions the band remains of sensibly constant width, indicating that in this case the solvation is probably very slight. The difficulty of drawing any definite conclusions from solutions of this salt lies in the fact that the solutions are not very stable, and hence the effects may very often be masked by chemical changes of unknown amount.

Chromium salts behave very much like those of nickel. Only two of them were studied in this work and these only in aqueous solution. The behavior of their bands is quite analogous to that of the green cobalt band, and hence calls for spectrophotometric study. Their diffuse character also makes them rather unfit for spectrographic investigations.

The most interesting and important results were obtained from the study of the salts of neodymium and praseodymium, especially those of the former. These substances have not only very many absorption bands, but they are remarkably narrow and sharp, and hence peculiarly suitable for spectrographic study.

The chief experimental results were the following:

1. The absorption spectra of aqueous solutions of the chloride and bromide of neodymium change very little with change in concentration, and the two are nearly identical throughout, excepting for the fact that the absorbing power of the bromide appears to be somewhat greater than that of the chloride.

2. The absorption spectrum of aqueous solutions of neodymium nitrate is somewhat different from that of the chloride or bromide, especially if the solutions are concentrated. With decrease in concentration the spectrum changes so as to become more and more nearly identical with that of the other salts. Certain bands, therefore, increase in intensity when the conditions for Beer's law obtain. Others decrease and remain constant only when molecules are kept constant.

Examples of the first class of bands are those at λ 4275, λ 4330, and λ 5205. Examples of the second kind are the bands at λ 4282 and λ 5235.

3. Addition of large amounts of calcium or aluminium chloride to a solution of neodymium chloride does not affect the spectrum appreciably, except the shading of the yellow band, and perhaps very slightly that of the green bands.

4. Solutions of the salts in nonaqueous solvents give spectra which are not only different for different salts, but the spectrum of any one salt is different in the different solvents. The spectra of neodymium or praseodymium chloride in methyl and ethyl alcohols, which are almost exactly alike, are apparent exceptions.

5. When neodymium chloride is dissolved in mixtures of water and one of the nonaqueous solvents, and the relative amounts of the two solvents in the mixture are varied, no marked change in the spectrum is observed when the amount of water is changed from 100 per cent to about 15 or 20 per cent. As the amount of water is still further reduced we find that the solution gives a spectrum which consists of a superposition of the spectra belonging to the aqueous and the nonaqueous solutions; the former decreasing in intensity while the latter increases as the amount of water is decreased. The composition of the mixed solvent which will show the two spectra with about half their normal intensity depends upon the concentration of the salt in solution, and a constant ratio between the number of molecules of water and those of the dissolved salt was indicated by the experiments; this ratio has the value 10.

Neodymium nitrate dissolved in mixtures of water and one of the nonaqueous solvents shows exactly the same change as the chloride; but in addition we get the changes in the spectrum produced by the great change in the state of dissociation of the salt. The result is that the whole change is a much more gradual one, and hence is not nearly so striking as it is in the chloride or bromide solutions.

Praseodymium chloride dissolved in mixtures of water and methyl or ethyl alcohol shows, in general, the same kind

of change in the spectrum as neodymium chloride, but in addition there appears in the alcoholic solutions an entirely new band having no analogue in the aqueous solution. This new band in the ultraviolet is by far the most intense in the entire spectrum. It disappears entirely on the addition of water, having about half its normal intensity for a half-normal solution when the water content of the solvent is about 8 per cent.

These facts seem to us inexplicable on any other hypothesis than the one we have put forward, namely, that when a salt of one of these elements is dissolved in a solvent both the molecules of the salt and the ions formed from them become solvated, that is, they combine with a certain number of molecules of the solvent. In the case of cobalt and copper salts we found reasons for believing that a series of solvates of varying complexity was formed, while with the rare elements the spectrum points rather to the existence of only one definite solvate. A more extended study, including the changes in the spectrum produced by change in temperature, may, however, modify this conclusion somewhat.

Granting the existence of the solvates, the phenomena observed in the absorption spectra of neodymium and praseodymium admit of a perfectly natural explanation. As this explanation has already been given in full under the discussion of neodymium nitrate in water—Beer's law—we need not repeat any part of it.

PHYSICAL CHEMICAL LABORATORY,
JOHNS HOPKINS UNIVERSITY,
June, 1908.

BENZENESELENONIC ACID AND RELATED COMPOUNDS.

BY HOWARD WATERS DOUGHTY.

The work herein described was begun in the laboratory of the University of Wisconsin in 1906. As it was interrupted by the author's change of residence and considerable time has been lost on that account, it seems advisable to give an account of the work up to the present time.

Some years ago the writer was engaged in an investigation of certain aromatic sulpho acids,[1] and it seemed to him that an investigation of the analogous selenium compounds might lead to interesting results. It was decided to start with the simplest member of the series, benzeneselenonic acid, and to prepare it, if possible, by the use of benzene and selenic acid, and then to proceed to the study of the more complex acids corresponding to the sulphur compounds already mentioned.

In 1889 Chabrie[2] prepared a substance by the action of selenium tetrachloride on benzene in the presence of aluminium chloride, which he supposed was selenophenol, C_6H_5SeH. The substance crystallized in yellow needles, melting at 60°. He also tried the action of concentrated selenic acid on benzene and found that an acid was formed which gave a soluble barium salt. He did not investigate the acid further and gave no analysis of the barium salt.

Some years later Krafft and Vorster[3] showed that selenium is capable of replacing the SO_2 group in aromatic sulphones, and by means of this reaction they prepared diphenyl selenide, a colorless oil boiling at 301°–302°:

$$Se + C_6H_5.SO_2.C_6H_5 \longrightarrow (C_6H_5.SeSO_2.C_6H_5) \longrightarrow C_6H_5.Se.C_6H_5 + SO_2.$$

In the following year Krafft and Lyons[4] prepared selenophenol by the following method: Diphenyl selenide heated with selenium gave diphenyl diselenide, melting at 63°.5:

$$C_6H_5.Se.C_6H_5 + Se \longrightarrow C_6H_5.Se.Se.C_6H_5.$$

By reducing this substance with sodium and acidifying the product with sulphuric acid they obtained an oil boiling at 183°, which distilled unchanged in an atmosphere of carbon dioxide, but oxidized very rapidly in the air to diphenyl diselenide. Analysis and reactions showed the oil to be selenophenol. Evidently the substance obtained by Chabrie was diphenyl diselenide.

[1] THIS JOURNAL, **33**, 388.
[2] Bull. Soc. Chim. [2], **50**, 133; [3], **2**, 788.
[3] Ber. d. chem. Ges., **26**, 2813.
[4] *Ibid.*, **27**, 1763.

Krafft and Vorster[1] also showed that when diphenyl selenide is treated with bromine in ether solution a dibromide, $(C_6H_5)_2SeBr_2$, is obtained, which melts at 140° with decomposition. This, when treated with cold 15 per cent solution of sodium hydroxide, gives diphenylselenoxide, $C_6H_5.SeO.C_6H_5$, melting at 113°–114°, which, when treated with hydrochloric acid, forms the dichloride, $(C_6H_5)_2SeCl_2$, melting at 179°–180°. Diphenylselenoxide is also obtained directly from diphenyl selenide by oxidation with chromic acid in acetic acid solution.

Krafft and Lyons[2] also prepared diphenylselenone, $C_6H_5.SeO_2.C_6H_5$, by oxidation of diphenylselenoxide with potassium permanganate. The selenone loses oxygen when heated and yields diphenyl selenide, which forms diphenyl diselenide when heated with selenium, and diphenyl diselenide is changed by nitric acid to the nitrate of benzeneseleninic acid, $C_6H_5.SeO_2H.HNO_3$, which, when neutralized with ammonia and treated with silver (nitrate?) solution gave a crystalline precipitate of silver benzeneseleninate, $C_6H_5.SeO_2Ag$.

In 1906 Stoecker and Krafft[3] obtained a product which they describe as the hydrate of benzeneseleninic acid, $C_6H_5.SeO_2H.H_2O$, by treating diphenyl diselenide with nitric acid, precipitating the silver salt and treating it with the calculated amount of hydrochloric acid, and crystallizing the product. It melted at 122°–124°. They also prepared benzeneselenonic acid by the action of chlorine water on diphenyl diselenide, and from the silver salt they obtained what they considered to be a hydrate of the acid by precipitating the silver with hydrogen sulphide. They do not appear to have had the pure acid in hand, but prepared several of its salts. This work of Stoecker and Krafft came to my notice after the work herein recorded was well advanced, and, as the method here described is entirely different from theirs and there are certain differences in our results, it seems well to give my work in full, though not with any desire of depreciating the claims of Stoecker and Krafft to priority.

[1] *Loc. cit.*
[2] Ber. d. chem. Ges., **29**, 424.
[3] *Ibid.*, **39**, 2197.

EXPERIMENTAL.

Preparation of Selenic Acid.—The selenic acid used in this investigation was prepared from black stick selenium by the following method: The selenium was dissolved in boiling nitric acid (1:1). The solution was evaporated to dryness, the selenium dioxide dissolved in water, a little barium chloride added to remove sulphuric acid, and the solution filtered and evaporated to dryness. The selenium dioxide was then purified by sublimation, though this precaution is probably unnecessary so far as this investigation is concerned. The pure selenium dioxide was dissolved in water and a slight excess of silver nitrate solution was added. The white precipitate of silver selenite was filtered off and washed. The residue was suspended in water and an excess of bromine added. After standing overnight the silver bromide was filtered off on glass wool or asbestos and the clear dilute solution of selenic acid concentrated by evaporation in an open dish until the temperature rose to 150°. This fairly strong selenic acid was then further dehydrated by heating under diminished pressure (20 mm.) for 12 hours at 180°. The selenic acid thus obtained was perfectly clear and colorless and contained no trace of selenous acid. It had a specific gravity of 2.53.

The benzene used was anhydrous and free from thiophene. Concentrated selenic acid serves as a good test for thiophene in benzene. If thiophene is present a dark blue coloration—about the color of Prussian blue—appears at the zone of contact between the selenic acid and the benzene after standing a few minutes. If the thiophene has been removed no color appears for a long time in the cold, and then only a light brown.

Barium Benzeneselenonate.—Method I.: One hundred grams each of the selenic acid, sp. gr. 2.53, and pure benzene were placed in a 750 cc. Erlenmeyer flask connected with a return condenser, and heated continuously for 100 hours on a water bath. The contents of the flask, after heating, consisted of a layer of benzene, almost colorless and containing no appreciable amount of dissolved substance, and a heavier layer of selenic acid containing the products of the reaction. This

acid layer had about the consistency of molasses, and was dark red in color. After separating the two layers by means of a separating funnel, the acid layer was poured into an excess of barium carbonate suspended in a liter of water, and the mixture heated to boiling and filtered. The filtrate was exactly neutralized with barium hydroxide, phenolphthalein being used as indicator, and filtered again. It was then evaporated to dryness on the water bath. The solid residue was extracted by means of a Soxhlet apparatus with chloroform for several days to remove a clear syrupy substance which is one of the products of the reaction, but which has not yet been examined. The barium salt remaining was then purified by crystallization from water.

Method II.: Selenic acid, two parts, and benzene, one part, were heated in a sealed tube at 110° for 100 hours. The progress of the reaction could be watched and the equilibrium point ascertained by noting the disappearance of the benzene layer. There was pressure in the tube, doubtless due to the formation of by-products such as the one mentioned above. The acid layer was separated and the barium salt prepared as described under Method I. The product was the same in both cases.[1]

Barium benzeneselenonate crystallizes from water in small plates. If the crystals separate slowly from a cold or not too warm solution they contain 3 molecules of water. If the solution is very concentrated and near the boiling temperature the salt crystallizes with 2 molecules of water. That the water is very loosely combined is shown by the fact that the first samples, which were air-dried in the laboratory of the University of Wisconsin in midwinter, were anhydrous. The

[1] NOTE: In a preliminary report of this work, presented before the American Chemical Society in June, 1907, the statement was made that when benzene and selenic acid were heated in a sealed tube the barium salt obtained had the composition $(C_6H_5.SeO)_2Ba$. This statement was based on analyses of the salt giving the following results: Ba found, 28.69, 28.68, 28.26; calculated, 28.50. Se found, 33.58; calculated, 32.82. As it has been impossible to duplicate these results, although several attempts have been made, it seems probable that with the small quantity in hand in the first preparation there was some impurity and that the analyses were suggestive of the product $(C_6H_5SeO)_2Ba$ merely by a coincidence. In all subsequent preparations, with more perfect methods of purification, the product has always been barium benzeneselenonate.

hydrated specimens were obtained in this laboratory. It may be mentioned in passing that in Madison, Wis., in midwinter, the air contains very little moisture, so that calcium chloride is not visibly altered by exposure to the air of the laboratory. The salt burns with explosive violence when heated so that the analyses for barium were made by precipitating barium sulphate from a solution of the salt rather than in the usual manner by igniting and treating with sulphuric acid. The selenium was determined by adding ammonium persulphate and sulphuric acid to the filtrate from the barium sulphate precipitation, and heating until the cloudiness noticed at first disappeared. Sodium bisulphite and concentrated hydrochloric acid were then added and the solution boiled until all selenium was deposited. The selenium was weighed on a Gooch filter as usual. The following results were obtained:

Of the salt deposited from a warm, fairly strong solution, 0.2343 gram lost 0.0233 gram water when heated at 110°.

	Calculated for $(C_6H_5.SeO_3)_2Ba.3H_2O$.	Found.
H_2O	9.00	9.08

Of the salt separating from a boiling concentrated solution, 0.2627 gram lost 0.0157 gram when heated to 110°.

	Calculated for $(C_6H_5.SeO_3)_2Ba.2H_2O$.	Found.
H_2O	6.19	5.98

The anhydrous salt gave results as follows:

	Calculated for $(C_6H_5.SeO_3)_2Ba$.	Found. I.	II.	III.
Ba	25.16	25.51	25.27	24.85
Se	29.01	...	...	28.53

I. was a sample of the salt with $3H_2O$; II., a sample of the salt with $2H_2O$; III. was a sample of salt prepared in the University of Wisconsin in midwinter and air-dried. It did not lose weight when heated at 110°.

Benzeneselenonic Acid.—The calculated amount of 0.1 N sulphuric acid was added to the solution of a weighed amount of the barium salt described above, and the barium sulphate was filtered off. The filtrate was evaporated to a small vol-

ume and allowed to crystallize. No difference in the product could be detected, whether the evaporation was completed in the air of the laboratory or in a vacuum desiccator over sulphuric acid. Benzeneselenonic acid separated in bunches of colorless needles, which, after drying on a porous plate, melted sharply at 142°. After cooling and solidifying the melting point was unchanged. When heated to 180° carbon dioxide and water were given off. There was no perceptible decomposition below this temperature and the beginning of decomposition appeared very sharply at this point. Benzeneselenonic acid crystallizes from aqueous solution without water of crystallization. The crystals are somewhat hygroscopic and are very easily soluble in water and in alcohol, but not in ether or benzene.

0.2654 gram gave 0.3481 gram of CO_2 and 0.0748 gram of H_2O.

	Calculated for $C_6H_5.SeO_3H$.	Found.
C	35.08	35.76
H	2.92	3.12

0.3977 gram of the acid was neutralized with 0.1 N sodium hydroxide.

	Calculated for $C_6H_5.SeO_3H$.	Found.
0.1 N NaOH	19.38 cc.	19.40 cc.

Benzeneselenonic acid gives a silver salt which is fairly soluble in water, from which it crystallizes in white, wartlike masses.

Silver Selenophenolate.—This substance is easily obtained from benzeneselenonic acid by the following method: When a solution of benzeneselenonic acid is treated with the calculated amount of silver nitrate solution no precipitate appears, but on addition of sulphur dioxide a white precipitate is formed, which immediately becomes intensely yellow, resembling cadmium sulphide in appearance. This precipitate is odorless, and is completely insoluble in water, alcohol, or ammonia. It is not changed by the action of hydrochloric acid. It dissolves in potassium cyanide. It is oxidized by nitric acid to a soluble compound, and from this solution hy-

drochloric acid precipitates silver chloride. A combustion did not yield satisfactory results, as diphenyl diselenide distilled off, leaving the silver, and was found at the outlet of the combustion tube, having escaped decomposition. Krafft has mentioned the difficulty of burning diphenyl diselenide or substances that give it when heated.

0.1850 gram of the yellow compound gave 0.1007 gram of silver chloride.

	Calculated for C_6H_5SeAg.	Found.
Ag	40.91	40.92

When benzeneselenonic acid in solution is treated with reducing agents, such as hydrogen sulphide, sulphur dioxide, or, best, with zinc and hydrochloric acid, selenophenol is obtained as a yellow oil with an overpowering and most nauseating odor. This oil is easily extracted with ether or carbon tetrachloride, and when the solution is evaporated the selenophenol is rapidly oxidized in the air to diphenyl diselenide, which crystallizes in pale yellow, silky needles, melting at 63°. Krafft and Lyons give 63°.5. The odor of diphenyl diselenide is extremely disagreeable, but is not nearly so bad as that of selenophenol.[1]

Stoecker and Krafft[2] prepared benzeneselenonic acid by precipitating silver from silver benzeneselenonate by means of hydrogen sulphide and evaporating the filtrate. They state that they obtained a hydrate of the acid in this way, but give no melting point or analysis. From the description which they give it would seem that their product is different from that prepared by the method used by me.

Several attempts were made to prepare benzeneselenonyl chloride, but without success. The action of phosphorus pentachloride on barium benzeneselenonate is extremely violent, being attended with flashes of light. When the phos-

[1] The writer has already had occasion to record his experience with thiophenol as to its physiological effects (THIS JOURNAL, **33**, 393). The effect of selenophenol on the skin is very similar to that of thiophenol, forming blisters which itch intensely. After a time these dry up, the skin scales off, and there appears to be a deposit of red selenium beneath it. The odor of selenophenol is very penetrating and is nauseating beyond description.

[2] Ber. d. chem. Ges., **39**, 2197.

phorus pentachloride is used in chloroform solution the action is less violent, but the chloride was not obtained, nor was the amide obtainable by treating the reaction mixture with strong ammonia. In some experiments selenic acid was found, indicating a deep-seated change.

Benzeneseleninic Acid.—This acid was obtained by Stoecker and Krafft[1] by treating diphenyl diselenide with nitric acid. They prepared the silver salt and from that obtained what they describe as the hydrate of benzeneseleninic acid, $C_6H_5.SeO_2H.H_2O$, melting at 122°–124°, and certainly their analysis by combustion gave values indicating this composition. Nevertheless, it appears to me that the substance as obtained by me is not a hydrate, and it seems possible that Stoecker and Krafft may have had the acid and not the hydrate.

When benzeneselenonic acid is treated with strong hydrochloric acid a white crystalline precipitate is formed and chlorine is given off. 0.3974 gram benzeneselenonic acid was dissolved in about 5 cc. water in a small distilling flask. Hydrochloric acid gas was passed through the solution and thence into a distilling flask containing potassium iodide solution. The iodine liberated was determined by titration with sodium thiosulphate. 0.2207 gram iodine was liberated, corresponding to 0.0278 gram oxygen.

	Calculated for $C_6H_5.SeO_2H \longrightarrow C_6H_5.SeO_2H$.	Found.
O	7.79	7.00

The apparatus was filled with carbon dioxide before the introduction of the hydrochloric acid and the chlorine was swept out by a current of carbon dioxide. As the results of this experiment seemed to show that benzeneselininic acid was the principal product of the reaction between hydrochloric and benzeneselenonic acids, the experiment was repeated on a larger scale. After the reaction was completed the hydrochloric acid solution was poured off from the crystalline precipitate and the latter was dissolved in chloroform and thus separated from the remaining acid solution. The chloroform solution was evaporated to dryness on the water bath, leaving a reddish

[1] *Loc. cit.*

brown oil, most of which dissolved in water and was removed from the residual tarry product by filtering. When the solution was evaporated to a small volume and allowed to cool, an almost quantitative yield of beautifully crystallized benzeneseleninic acid was obtained. This was further purified by recrystallization from water, but the difference in melting point between the first and fourth fractions was not more than half a degree. The substance was dried in the air on porous plates, and melted at 122°. Benzeneseleninic acid is much more soluble in hot water than in cold and crystallizes in very thin rhombic plates. It melts at 122°, and after cooling and solidifying, still melts at very nearly the same point. Heated to 200° it decomposes, giving off a colorless gas. As Stoecker and Krafft had obtained a product which seemed to be a hydrate of this acid and yet had approximately the same melting point, 122°–124°, especial consideration was given to this point.

0.2042 gram of the acid required 10.72 cc. of 0.1 N barium hydroxide solution for neutralization.

	Calculated for $C_6H_5.SeO_2H.H_2O$.	Calculated for $C_6H_5.SeO_2H$.	Found.
0.1 N $Ba(OH)_2$	9.86 cc.	10.80 cc.	10.72 cc.
Ba, per cent,	33.09	36.24	35.94

Stoecker and Krafft found that when their hydrate was heated for three hours under 15 mm. pressure at 100° and finally at 130° it lost 8.36 per cent in weight, while the calculated loss was 8.69 per cent. Not having a vacuum desiccator that would stand heating, I placed the acid described above in a small distilling bulb and proceeded as in distillation under diminished pressure, using a pressure of about 50 mm. and heating at a uniform temperature of 130°. The loss in weight was determined and the remaining white solid dissolved in water and titrated with 0.1 N barium hydroxide. During the heating a white sublimate was observed just above the level of the distilling bath, and some of this was even carried over into the side tube of the distilling bulb. Evidently, this would account for a loss in weight if the substance were heated in the ordinary vacuum desiccator.

0.2458 gram of acid lost 0.0130 gram when heated in the manner just described. The residue, when dissolved in water, required 12.76 cc. 0.1 N $Ba(OH)_2$ for its neutralization. Compared with the titration of the original substance without heating, this amount of acid should require 12.78 cc., so there was no diminution of acidity on heating, and the white sublimate was probably the same as the portion that did not sublime. Two explanations are possible. Either the substance is a hydrate, as claimed by Stoecker and Krafft, and yields the acid when heated, or the original substance is an acid, as shown by titration, and yields an anhydride on heating. The amount of water lost by my sample is little more than half that required by the first hypothesis.

Benzeneseleninic Anhydride.—In order to test this point portions of benzeneseleninic acid were heated at 130° in an air bath under atmospheric pressure. No constant weight could be obtained although the substance was heated for over 30 hours in the aggregate. Moreover, it was found that if it were left exposed to the air it took up very nearly as much moisture as it had lost during the heating. These facts are easily explained on the basis of the formation of an anhydride that sublimes at a temperature of about 130°. A portion of the substance that had been heated for 30 hours at 130° was dissolved in water and titrated with 0.1 N barium hydroxide. The portion originally weighed 0.1826 gram. After heating it weighed 0.1418 gram and required 7.94 cc. 0.1 N $Ba(OH)_2$ to neutralize it.

	Calculated for			
	$C_6H_5.SeO_2H.H_2O$.	$C_6H_5.SeO_2H$.	$(C_6H_5.SeO)_2O$.	Found.
0.1 N $(BaOH)_2$	6.85 cc.	7.50 cc.	7.88 cc.	7.94 cc.

A portion of the anhydride was placed while hot in a melting point tube and the tube was sealed. The substance melted sharply at 164° with no sign of decomposition, and after cooling and solidifying the melting point was unchanged.

I therefore conclude that when benzeneselenonic acid is treated with concentrated hydrochloric acid in the cold, benzeneseleninic acid is precipitated, and when this acid

crystallizes from water it does so without water of crystallization. When benzeneseleninic acid is heated at 130°, either in a vacuum or under atmospheric pressure, it forms benzeneseleninic anhydride, melting at 164°, which is not changed by heating at its melting point but decomposes at 200°. The anhydride is exceedingly hygroscopic, and if left exposed to the air it absorbs moisture, forming benzeneseleninic acid. The anhydride sublimes at about 130°.

The work on the aromatic oxygen acids of selenium will be continued in this laboratory.

AMHERST COLLEGE,
February 10, 1909.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXVI.—RESEARCHES ON THIOCYANATES AND ISOTHIOCYANATES: A NEW CLASS OF ISOTHIOCYANATES. ISOTHIOCYAN ETHERS.

[EIGHTH PAPER.]

BY TREAT B. JOHNSON AND HERBERT H. GUEST.

This paper is a contribution to our knowledge of the action of potassium thiocyanate on primary alkyl halides. By the term primary halide is meant any derivative of methyl chloride, bromide, or iodide of the general formula I., in which R can represent any saturated or unsaturated organic radical:

$R.CH_2.hal.$	$(R)_2CH.hal.$	$(R)_3C.hal.$
I.	II.	III.

We have investigated, in this laboratory, the action of potassium thiocyanate on about eighteen different halides of this type I., besides several secondary (II.) and tertiary (III.) halides.[1] The incentive for this study was to ascertain what influence, if any, the positive or negative character of the radicals substituted for R had in determining the formation of thiocyanates and isothiocyanates. We have substituted for R in primary halides saturated and unsaturated alkyl

[1] J. Am. Chem. Soc., **23**, 283; **24**, 439, 680, 743; **28**, 1454. THIS JOURNAL, **26**, 345; **38**, 456.

and aryl groups, ester, acidamide, and diacidamide groupings, but in no case have we obtained a primary halide which reacts with potassium thiocyanate to give an isothiocyanate.

The only acyclic groups, so far as the writers are aware, which produce conditions favorable to the formation of isothiocyanates, when substituted for R in primary halides (I.), are the vinyl group $CH_2:CH$ or derivatives of this unsaturated radical. For example: allyliodide,[1] IV., and chlorallyl chloride,[2] V., react with potassium thiocyanate, giving thiocyanates

$CH_2:CH.CH_2I$ (IV.) $\qquad$ $CH_2:CCl.CH_2Cl$ (V.)

which rearrange smoothly into isothiocyanates when heated.

A careful review of the literature[3] reveals the fact that apparently the action of potassium thiocyanate on halogen substituted ethers has not been investigated.[4] As we had occasion to continue the study of the behavior of potassium thiocyanate towards alkyl halides, it seemed of interest to investigate the action of some known, primary chlormethyl ethers of the general formula $ROCH_2Cl$, in which R represents an alkyl radical, *viz.*, CH_3, C_2H_5, etc.

We have now made the interesting observation that chlordimethyl ether,[5] VI., chlormethylethyl ether,[6] VII., and chlormethylisoamyl ether,[7] VIII., react practically quantitatively with potassium thiocyanate, giving the corresponding isothiocyanates, IX., X., and XI:

[1] Billeter: Ber. d. chem. Ges., **8**, 464. Gerlich: Ann. Chem. (Liebig), **178**, 89.

[2] Henry: Ber. d. chem. Ges., **5**, 188.

[3] Beilstein's Handbuch.

[4] Sommelet (Compt. rend., **143**, 827) and Gauthier (*Ibid.*, **143**, 831) have recently shown that the chlormethyl ethers react smoothly with mercuric, silver, and cuprous cyanides, giving the corresponding nitriles, $ROCH_2.CN$. They also combine smoothly with the alkali salts of organic acids, giving compounds of pharmaceutical value. [Patent (No. 137585) der Farbenfabriken vorm. Friedr. Bayer und Co., "Darstellung der Salicylsäurealkyloxymethylester aus Chlormethylalkyläthern und Salicylaten." This compound, o-$HO.C_6H_4.CO_2.CH_2OCH_3$, is used as an antirheumatic. Wedekind: Ber. d. chem. Ges., **36**, 1383.]

[5] Friedel: Bull. Soc. Chim., **28**, 171. Kleber: Ann. Chem. (Liebig), **246**, 97. Henry: Bull. Acad. Roy. Belgique [3], **25**, 439; Ber. d. chem. Ges., **26**, Ref. 933. Favre: Bull. Soc. Chim. [3], **11**, 879; Compt. rend., **119**, 284.

[6] de Gaspari: Gazz. chim. ital., **27**, II., 297.

[7] Favre: *Loc. cit.*

CH_3OCH_2Cl	$C_2H_5OCH_2Cl$	$C_5H_{11}OCH_2Cl$
VI.	VII.	VIII.
↓	↓	↓
CH_3OCH_2NCS	$C_2H_5OCH_2NCS$	$C_5H_{11}OCH_2NCS$
IX.	X.	XI.

The isothiocyanate structure is established by the facts that these compounds are desulphurized by warming with an alkaline solution of lead acetate, and react with thiobenzoic acid with formation of carbon bisulphide. They also combine smoothly with ammonia and organic bases, giving derivatives of a new class of thioureas—$R'NHCSNHCH_2OR$.

Our observation that the primary chlormethyl ethers react with potassium thiocyanate, giving isothiocyanates, is in accord with the experimental evidence which has been brought forward in previous papers from this laboratory.[1] The results do not conform to the theory[2] that a strong, negative character favors the formation of isothiocyanates. The benzoyl—C_6H_5CO—and carbethoxy—$COOC_2H_5$—radicals have a more negative influence than methoxy (—OCH_3), nevertheless their substitution in primary halides[3] produces a condition which is unfavorable for the formation of isothiocyanates.

$CH_3.CH_2Cl$	$CH_3O.CH_2Cl$	$C_2H_5OOC.CH_2Cl$	$C_6H_5CO.CH_2Cl$
↓	↓	↓	↓
$CH_3CH_2.SCN$	$CH_3OCH_2.NCS$	$C_2H_5OOCCH_2SCN$	$C_6H_5COCH_2SCN$

Previous results[4] have indicated that possibly an unsaturated condition, as well as a negative character, is required for the formation of isothiocyanates. The facts that the saturated radicals, *viz.*, methoxy-, ethoxy-, and isoamoxy-, and the unsaturated vinyl group $CH_2:CH$ produce conditions favorable for the formation of isothiocyanates show that the idea of the influence of unsaturated condition of the molecule is not

[1] *Loc. cit.*

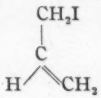
[2] Michael: J. prakt. Chem., **37**, 509 (1888). Dixon: J. Chem. Soc., **75**, 390 (1889).

[3] Aripides: Ann. Chem. (Liebig), **249**, 10; Obaegia: *Ibid.*, **266**, 326; Dyckerhoff: Ber. d. chem. Ges., **10**, 120.

[4] *Loc. cit.*

of wide application. A similar unsaturated condition exists in benzyl chloride, XII., as in allyl iodide, XIII., but the former gives a thiocyanate,[1] while the latter forms an isothiocyanate.[2]

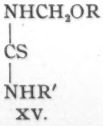
XII.



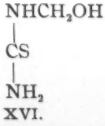
XIII.

XIV.

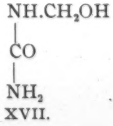
The etherthioureas, XV., which are formed by the action of the isothiocyan ethers on amines, are well crystallized compounds and stable at ordinary temperature. They are derivatives of the unknown oxymethylthiourea, XVI. The corresponding oxygen compound, oxymethylurea, XVII., has recently been prepared by Einhorn and Hamburger[3] by condensing formaldehyde with urea in presence of barium hydroxide. Some characteristic transformations of this new class of thioureas, XV., will receive attention in a later publication.



XV.



XVI.



XVII.

Experimental Part.

Isothiocyandimethyl Ether, $CH_3.OCH_2NCS$.—Fifty-two grams of chlordimethyl ether, dissolved in 100 cc. of anhydrous benzene, were digested with 75 grams of dry potassium thiocyanate, at 110°, for two days. After being filtered from potassium chloride and potassium thiocyanate, and freed from the excess of benzene at 120°–130°, the isothiocyanate was

[1] Ber. d. chem. Ges., **2**, 637; **5**, 689.
[2] *Loc. cit.*
[3] Ber. d. chem. Ges., **41**, 24.

purified by distillation under diminished pressure. It boiled at 56°–60° at 30 mm. and at 138° at 770 mm. The isothiocyanate is a colorless oil which has an irritating odor and attacks the eyes. Analysis (Kjeldahl):

	Calculated for C_3H_5ONS.	Found.
N	13.5	13.13

Isothiocyanmethylethyl Ether, $CH_3CH_2OCH_2NCS$.—This compound was prepared by digesting chlormethylethyl ether in benzene with potassium thiocyanate for about 40 hours at 120°–130°. It boiled at 93°–97° at 97–100 mm. pressure. The yield was excellent. The isothiocyanate is a colorless oil, which has an unpleasant odor and attacks the eyes, producing tears. It is very stable at ordinary temperature, and underwent no change after preservation for five months. It reacts with thiobenzoic acid at 100° with evolution of carbon bisulphide.

Analysis (Kjeldahl):

	Calculated for C_4H_7ONS.	Found.
N	11.96	11.55

Isothiocyanmethylisoamyl Ether, $C_5H_{11}.O.CH_2.NCS$.—This isothiocyanate was prepared under the same conditions as the two preceding isothiocyanates. From 140 grams of the chlormethylisoamyl ether we obtained 100 grams of the isothiocyanate boiling at 111°–114° at 22–23 mm. pressure. It boiled, under ordinary pressure, at 208°–210°, and at 122°–125° at 34 mm. pressure. This isothiocyanate appears to be less stable than the corresponding methyl and ethyl derivatives and slowly deposits a yellow substance on long exposure to the air.

Analysis:

0.0981 gram of substance gave 7.4 cc. N at 19°.5 and 773 mm.

	Calculated for $C_7H_{13}ONS$.	Found.
N	8.81	8.80

Behavior of Isothiocyanmethylisoamyl Ether towards Thiobenzoic Acid.—About 6.0 grams of the isothiocyanate and the

calculated proportion of thiobenzoic acid were dissolved in benzene, and the solution heated for several hours on the steam bath.

The excess of benzene was then distilled off and mixed with an alcoholic solution of potassium hydroxide and some copper sulphate. We obtained at once a heavy, yellow precipitate of copper xanthate, indicating the presence of carbon bisulphide. The product of the reaction was a heavy, viscous oil which finally deposited about 0.1 gram of yellow, crystalline material on long standing. This substance was insoluble in an aqueous solution of sodium hydroxide and contained sulphur. It crystallized from 95 per cent alcohol in prismatic crystals which melted at 160°–161° to an oil without effervescence. A nitrogen determination (Kjeldahl) agreed with the calculated value for a polymeric form of *isothiocyanmethylisoamyl ether*, $(C_5H_{11}.O.CH_2.NCS)_x$.

	Calculated for $(C_7H_{13}ONS)_x$.	Found.
N	8.81	8.92

Ethoxymethylthiourea, $C_2H_5.O.CH_2NHCSNH_2$.—Some isothiocyanmethylethyl ether was poured into an excess of strong, aqueous ammonia and the mixture shaken vigorously until the isothiocyanate completely dissolved. The solution was then heated on the steam bath, in a good draught, to remove the ammonia and water as quickly as possible. We obtained a viscous, hydroscopic oil which immediately solidified on cooling. After washing with ether the thiourea melted at 92°–93° to a clear oil. The compound is very soluble in water and alcohol and apparently undergoes decomposition by protracted heating with these solvents. It crystallized from benzene in plates.

Analysis (Kjeldahl):

	Calculated for $C_4H_{10}ON_2S$.	Found.
N	20.9	21.5

1-Phenyl-2-ethoxymethylthiourea, $C_6H_5NHCSNHCH_2OC_2H_5$.—This thiourea was prepared by dissolving 3.0 grams of isothiocyanmethylethyl ether in anhydrous ether and then adding

the calculated amount of aniline (2.4 grams). Reaction took place with evolution of heat, causing the ether to boil, and the thiourea separated in colorless crystals. It is very soluble in hot ethyl alcohol but deposits, on cooling, in six-sided plates, or tabular crystals, melting at 125°–126° to a clear oil.

Analysis:

0.1320 gram substance gave 15 cc. N at 21° and 772 mm.

	Calculated for $C_{10}H_{14}ON_2S$.	Found.
N	13.33	13.14

1-Paratolyl-2-ethoxymethylthiourea, $CH_3C_6H_4NHCSNHCH_2OC_2H_5$.—A quantitative yield of this thiourea was obtained when 4.5 grams of *p*-toluidine were dissolved in ether with 5.0 grams of isothiocyanmethylethyl ether. It crystallized from ethyl alcohol in plates melting at 120° to an oil.

Analysis (Kjeldahl):

	Calculated for $C_{11}H_{16}ON_2S$.	Found.
N	12.50	12.49

Action of Aqueous Ammonia on 1-Paratolyl-2-ethoxymethylthiourea.—Two grams of the thiourea and about 8–10 cc. of strong, aqueous ammonia were heated at 140°–150° for 2 hours. There was some pressure when the tube was opened and a clear, colorless solution was obtained. After concentration of this solution, and cooling, we obtained a good yield of material in glistening plates. They melted at 41°–42° and were soluble in dilute acids and insoluble in alkalis. The compound was identified as *p*-toluidine. A mixture of the substance and pure *p*-toluidine melted at 42°–43°.

1-Phenyl-2-isoamoxymethylthiourea, $C_6H_5NH.CSNHCH_2OC_5H_{11}$. — From isothiocyanmethylisoamyl ether and aniline. It is extremely soluble in warm isoamyl alcohol but separates, on cooling, in rhombic plates melting at 109° to an oil.

Analysis (Kjeldahl):

	Calculated for $C_{13}H_{20}ON_2S$.	Found.
N	11.11	10.96

1-Paratolyl-2-isoamoxymethylthiourea, $CH_3.C_6H_4NHCSNHCH_2OC_5H_{11}$.—A quantitative yield of this thiourea was obtained when *p*-toluidine and isothiocyanmethylisoamyl ether, in molecular proportions, were dissolved in ether. It crystallized from isoamyl alcohol in plates melting at 119°.

Analysis (Kjeldahl):

	Calculated for $C_{14}H_{22}ON_2S$.	Found.
N	10.53	10.40

Action of Aqueous Ammonia on 1-Paratolyl-2-isoamoxymethylthiourea.—When this thiourea was heated with aqueous ammonia at 140°–150° it was decomposed with formation of *p*-toluidine melting at 42°.

1,1-Methylphenyl-2-isoamoxymethylthiourea, $(CH_3)\ (C_6H_5)N.CSNHCH_2OC_5H_{11}$.—Prepared from isothiocyanmethylisoamyl ether and monomethylaniline. It crystallized from isoamyl alcohol in stout, well-developed prisms melting at 87°.

Analysis (Kjeldahl):

	Calculated for $C_{14}H_{22}ON_2S$.	Found.
N	10.53	10.13

NEW HAVEN, CONN.,
January 18, 1909.

NOTE ON SOLUBILITY DETERMINATIONS WITH THE REFRACTOMETER.

BY FREDERICK H. GETMAN AND F. B. WILSON.

In a recent paper on the "Determination of the Solubility of a Given Substance by Means of Pulfrich's Refractometer,"[1] Osaka shows that the relation between the angles of refraction of a mixture and its components may be simply expressed by the equation

$$ax + bx^2 = \delta - \delta_1 = \Delta,$$

where δ and δ_1 represent the angles directly observed on the

[1] Memoirs College Sci. Eng., Kyoto Imperial Univ., **1**, 265 (1906–7).

divided circle of the refractometer when a solvent and solution are examined, x the quantity of solute in grams per 100 cc. or 100 grams of solution, and a and b constants.

Solving this equation for x we have

$$x = -\frac{a}{2b} \pm \frac{\sqrt{\frac{a^2}{4b} - \Delta}}{b} \qquad (1),$$

where the lower sign is taken if a and b have opposite signs.

The author claims that this empirical formula is more convenient and reliable than the well-known relation

$$100(n - 1)/d = p_1(n_1 - 1)/d_1 + p_2(n_2 - 1)/d_2,$$

where n and d denote the index of refraction and density of a mixture and n_1, n_2,..... and d_1, d_2,..... the corresponding magnitudes of the components whose percentage amounts are p_1, p_2,.....

In his paper the author applies the formula to solutions of benzophenone in alcohol, potassium chloride in water, and ethyl ether in water. In each of these cases the agreement between observed and calculated values is good for the more concentrated solutions but the percentage error increases rapidly with the dilution.

In concluding his paper Osaka emphasizes the simplicity and convenience of the method and calls attention to the fact that it can be used for solubility determinations where ordinary methods fail.

Having at hand considerable data from a recent study of the refractive indices of aqueous solutions[1] it seemed of interest to us to further test the validity of Osaka's formula and at the same time to compare it with an equation expressing the concentration of a solution as a simple linear function of its index of refraction.

If the refractive indices of a series of solutions of the same solute are plotted against the corresponding concentrations it is found that the points so obtained all lie approximately on the same straight line. If N_w denotes the refractive index

[1] THIS JOURNAL, **40**, 468 (1908).

of the solvent at the same temperature as that at which the index of the solution is measured and N_s denotes the refractive index of the solution containing x grams of solute in 100 cc. of the solution, then

$$x = \frac{N_s - N_w}{\alpha} \qquad (2),$$

where α is the constant of the straight line equation.

In the accompanying tables the following notation is used:

x = number of grams of solute in 100 cc. of solution,
δ = observed angle on divided circle of refractometer,
N_s = index of refraction of solution for sodium light,
x_1 = concentration of solution calculated by formula (1),
x_2 = concentration of solution calculated by formula (2),
a and b = constants in formula (1),
α = constant in formula (2).

Table I.—Potassium Chloride. $t = 20°.7$.

$a = 0.284$ $b = 0.0019$ $\alpha = 0.001260$

x.	δ.	N_s.	x_1.	x_2.
20	62°20′	1.35764	...	...
16	63°13′	1.35301	15.89	15.81
10	64°35′	1.34603	...	...
6	65°36′	1.34096	6.07	6.26
2	66°32′	1.33648	2.60	2.68

Table II.—Potassium Bromide. $t = 21°.9$.

$a = 0.248$ $b = 0.0012$ $\alpha = 0.001120$

x.	δ.	N_s.	x_1.	x_2.
40	58°52′	1.37655	42.6	38.8
30	60°45′	1.36613	30.8	29.5
20	62°46′	1.35536	...	...
15	63°48′	1.35000	...	...
8	65°21′	1.34221	8.0	8.14
6	65°50′	1.33984	6.26	6.02
4	66°18′	1.33759	3.9	4.01
3	66°30′	1.33663	3.1	3.15

Table III.—Potassium Iodide. $t = 20°.5$.

$a = 0.275$ $b = 0.000883$ $\alpha = 0.001265$

x.	δ.	N_3.	x_1.	x_2.
80	49°30′	1.42155	88.12	77.83
40	57°40′	1.38334	...	...
30	59°48′	1.37134	...	...
16	63° 8′	1.35344	14.32	16.08
15	63°20′	1.35241	13.42	15.27
8	65° 5′	1.34353	6.72	8.25
6	65°37′	1.34090	4.62	6.17
3	66°23′	1.33719	1.82	3.24

Table IV.—Potassium Nitrate. $t = 20°.7$.

$a = 0.204$ $b = 0.0016$ $\alpha = 0.000876$

x.	δ.	N_3.	x_1.	x_2.
20	63°43′	1.35043	20.67	19.79
15	64°33′	1.34619	...	...
10	65°22′	1.34187	...	...
6	66° 7′	1.33850	5.91	6.22
4	66°25′	1.33705	4.22	4.52
3	66°37′	1.33608	3.18	3.41
2	66°48′	1.33521	2.26	2.42
1	67°	1.33426	1.25	1.33

Table V.—Potassium Chloride. $t = 20°.1$.

$a = 0.2375$ $b = 0.0125$ $\alpha = 0.000914$

x.	δ.	N_3.	x_1.	x_2.
6	66°10′	1.33823	7.53	5.26
5	66°21′	1.33735	5.23	4.66
4	66°30′	1.33663	....	....
3	66°39′	1.33592	....	....
2	66°50′	1.33505	1.98	2.14
1.5	66°55′	1.33465	1.51	1.70
1	67°	1.33426	1.12	1.28

Table VI.—Potassium Chromate. $t = 19°.8$.

$a = 0.442$ $b = 0.0041$ $\alpha = 0.002012$

x.	δ.	N_S.	x_1.	x_2.
40	53°25′	1.40811	46.23	37.28
30	56°19′	1.39110	37.98	28.83
20	59°30′	1.37301	...	...
15	61°14′	1.36351	...	...
8	63°50′	1.34983	8.30	8.32
6	64°37′	1.34586	6.17	6.34
4	65°28′	1.34163	4.10	4.24
3	65°52′	1.33968	3.10	3.27

Table VII.—Cane Sugar. $t = 24°.5$.

$a = 0.3018$ $b = 0.000917$ $\alpha = 0.001424$

x.	δ.	N_S.	x_1.	x_2.
40	56°32′	1.38985	40.51	39.86
30	59° 1′	1.37572	...	...
20	61°35′	1.36163	...	...
10	64°21′	1.34736	9.96	10.02
7.09	65°10′	1.34311	7.02	7.04
4	66° 4′	1.33871	4.06	3.95
3.55	66°15′	1.33783	3.36	3.34
1.42	66°52′	1.33489	1.28	1.26
0.57	67° 7′	1.33371	0.48	0.44

Inspection of the data recorded in the preceding tables shows that the refractometric method for solubility determination gives at best only approximate results.

The observation of Osaka that the percentage error is greatest in the more dilute solutions is confirmed.

This failure of the formula with dilute solutions is probably to be attributed to the preponderating influence of the solvent on the optical properties of the solution.

A comparison of the results obtained by formulas (1) and (2) shows that the latter is quite as satisfactory as the former.

Furthermore formula (2) is not empirical and involves less laborious calculations.